

SIMULATION AND EXPERIMENTAL VALIDATION OF  
RADICAL POLYMERIZATION WITH AIBN INITIATOR IN  
PRESENCE OF SHEAR

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CERTIFICATE

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## ABSTRACT

The effect of shear on the rate of polymerization of styrene in presence of activated carbon has been studied. It was found that the rate of polymerization decreases in presence of shear and is enhanced in presence of activated carbon. Based on the chemistry, a kinetic model has been proposed in which carbon is participating in the polymerization and is found to describe the experimental results well. We have also carried out simulation of free radical polymerization. Analytical expressions for isothermal polymerization have been developed for monomer and polymer concentrations and for moments of radical and dead polymer distributions in terms of a dimensionless variable  $Z$ . The analytical solution has later been adopted for nonisothermal polymerization in presence of gel effect.

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## NOMENCLATURE

A, B	terms in $D_0$ equation (Table 11)
$C_1, C_2$	Constants in $Q_1$ equation (eqn 36)
$C^*$	Constant in $Q_2$ equation (eqn 48)
$C_P$	Specific heat at constant pressure
D	inside diameter of reactor
$E_d, E_p, E_t$	activation energies of initiation, propagation and termination reactions in absence of gel and glass effect
$E_{\theta t}, E_{\theta p}, E_{\gamma}$	energies in $\theta_t, \theta_p, \gamma$ expression (Table 11)
f	initiator efficiency
$\Delta H_r$	enthalpy of propagation reaction
$I_2$	initiator
$I_0(z), I_1(z),$	Modified Bessel functions
$K_0(z), K_1(z)$	
$K_{\gamma}^0$	frequency factor in $\gamma$ expression
$k_{po}, k_{to}$	rate constants for propagation and termination
$k_d$	rate constant for initiation
$k_d^0, k_p^0, k_t^0$	frequency factors for $k_d, k_{po}$ and $k_{to}$
$k_p, k_t$	rate constants for propagation and termination (with gel effect)
$k_{tc}, k_{td}$	termination rate constants for combination and disproportionation ( $k_{tc} + k_{td} = k_t$ )
m	$k_p/k_t$
M	Monomer

$M_w$	Molecular weight of monomer
$P_n$	growing radical having $n$ repeating units
$Q_i$	$i^{\text{th}}$ moment of polymer radical distribution
$I, I_1$	primary and secondary radicals
$r_p$	rate of polymerization
$R$	universal gas constant
$R_R, R_G$	radius of rotor and glass cylinder
$T$	Temperature, K
$T_{gp}$	glass transition temperature of polymer, K
$T_w$	Temperature at wall, K
$t$	reaction time
$U$	overall heat transfer coefficient
$x$	related to time of polymerization
$Y$	related to $r_p$ (eqn 3)
$Z$	dimensionless variable (eqn 13)

### Greek letters

$$\begin{aligned}
 \alpha &= \frac{(-\Delta H_r) [M]_0 m}{\rho C_p} \\
 \beta &= \frac{\rho C_p}{D \rho C_p f k_d Z_0} \\
 \gamma &= \frac{k_{tc}/k_{td}}{\frac{\omega R_R}{R_G - R_R}} \\
 \omega &= \text{angular velocity}
 \end{aligned}$$

$\theta_t, \theta_p$	characteristic migration times
$\theta_t^0, \theta_p^0$	pre exponential factors for $\theta_t$ and $\theta_p$
$\lambda_i$	$i^{\text{th}}$ moment of dead polymer distribution
$\lambda_{i0}$	$i^{\text{th}}$ moment of dead polymer distribution at time $t=0$
$\phi_p$	volume fraction of polymer in reaction mixture
$\rho_m$	density of monomer
$\rho_p$	density of polymer
$\rho_{ps}$	density of polystyrene
$\psi$	$\frac{1 - [P]_0^*}{1 + [P]_0^*}$

### Symbols

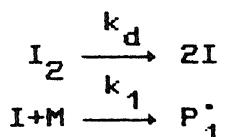
$[C]$	Concentrations, gmol/lit
$[C]_0$	feed concentration, gmol/lit
$[C]_s$	Concentration with QSSA valid
$[C]_0^*$	ratio , $\frac{[C]_0}{[C]_s}$

## CHAPTER 1

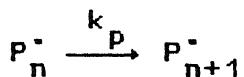
### Introduction

The chain growth polymerization has been studied in detail and has been shown to consist of initiation, propagation and termination steps. These can be schematically written as

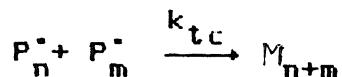
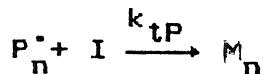
Initiation:



Propagation:



Termination:



(1)

As can be seen above, the initiation is a sequential reaction of decomposition of initiator molecules to give primary radicals and subsequent combination of primary radicals with monomer molecules. In reality all primary radicals do not produce propagating chains and they remain in 'cages' consisting of surrounding molecules before they diffuse apart. However before this diffusion takes place, the primary radicals may react with one another to form an inactive species. In order to account for this recombination, a factor called initiator efficiency,  $f$  is introduced. There are several factors which

affect the initiator efficiency and these have been discussed in the literature in detail<sup>14-18</sup>.

In the propagation reaction, the monomer adds on to the polymer radical and the propagation rate constant  $k_p$  has been assumed to be independent of chain length. Polymer radicals may be converted into polymer molecules by primary and mutual (combination and disproportionation) termination. The expression for rate of polymerization is obtained by making use of the standard kinetic assumption of a steady state approximation of transient species, namely, the chain radicals. Thus we obtain.

$$r_p = k_p \left[ \frac{f k_d [I_2]}{(k_{tc} + k_{td})} \right]^{1/2} [M] \quad (2)$$

This equation is valid only for low conversions and it will be shown later that the Quasi Steady State Approximation (QSSA) breaks down due to the gel and glass effects.

A parameter  $y$  independent of monomer and initiator concentration may be defined as

$$y = \frac{r_p}{[M][I_2]^{1/2}} \quad (3)$$

The rate of polymerization at low conversions, in the absence of shear for several monomers have been determined experimentally and excellent compilations are available<sup>5</sup>. Studies have been carried out establishing the effect of mixing upon the rate of polymerization in which simple stirring devices were used. However, no correlation exists which relates the rate of polymerization with shear rates. In this work we have studied

the effect of shear on the rate of polymerization of styrene using azo iso butyronitrile (AIBN) as the initiator. We have also studied the effect of activated carbon of various particle size on the rate of polymerization.

It is well established that after certain conversion, the 'gel effect' appears as a sharp increase in the rate of reaction, usually accompanied by an increase in molecular weight and viscosity. The gel effect occurs after about 10% conversion depending on the temperature and the amount of initiator used. Numerous theoretical and experimental studies of the gel effect have been reported and it is generally agreed that it is due to the reduction in the termination rate constants,  $k_{tc}$  and  $k_{td}$ <sup>19-28</sup>. After a conversion of 70-80% is reached, the reaction mass becomes highly viscous and the chain propagation becomes diffusion controlled. As a result of reduction in  $k_p$ , the rate of polymerization goes down as the reaction temperature approaches the glass transition temperature of the polymerizing mixture. This behaviour is known as the glass effect<sup>29-33</sup>.

Most of the studies of chain growth polymerization in reactors assume isothermal reactor operation. In commercial practice however, reactors cannot be maintained in isothermal conditions. Practical problems of heat transfer and thermal runaway invariably occur<sup>34-46</sup>. Because of their simplicity and low costs, tubular reactors are commercially employed and in the literature they have been theoretically as well as experimentally investigated<sup>35-42</sup>.

In earlier studies of free radical polymerization, it was common to assume that the quasi steady state approximation holds.

Under this approximation, the rate of formation and rate of depletion of the polymer radicals are equal. Therefore,

$$k_t [P]_s^2 = 2fk_d [I_2] \quad (4)$$

Here  $[P]_s$  represents the total concentration of polymer radicals with QSSA valid and  $[I_2]$  is the initiator concentration. However, when gel effect sets in,  $k_t$  has been shown to decrease in value, which will result in increased  $[P]_s$  under QSSA, this way leading to higher rates of polymerization. Since all polymerization reactions are exothermic in nature, the temperature of the polymer mass would go up for the same cooling rate which in turn would give higher rate of initiation. Hence under the influence of gel effect, the upward thermal drift always occurs and the QSSA breaks down.

If the QSSA breaks down, the mole balance relation for polymer radicals  $[P]$  would be governed by a nonlinear first order differential equation instead of the simple relation given in eqn (4). The concentration  $[P]$  in the reaction mass is normally a very small number compared to the monomer or initiator concentration. As an example, for styrene polymerizing at  $60^\circ\text{C}$  with benzoyl peroxide initiator,  $[P]_s$  (as calculated from eqn (4)) is of the order  $10^{-8}$  moles per liter. As a consequence in the numerical computation of  $[P]$  through its governing differential equation, the time increment  $\Delta t$  must be chosen very small. This would mean that the differential equations governing the performance of the tubular reactor carrying out radical polymerization are numerically extremely 'stiff' and the numerical solution is computationally time consuming.

In this work, we have written down the transient mole

balance relation for all species in the reaction mass. Assuming various rate constants for the mechanism of isothermal free radical polymerization given in eqn (1) as time independent, we develop the complete analytical solution. We have also integrated the energy balance equation making use of the above assumption. After every time step  $\Delta t$  we estimate the temperature, and rate constants are evaluated at the new temperature which are made use of in calculating  $[M]$ ,  $[P]$  and other quantities in the next time step. This removes the stiffness of the differential equation and results are obtained conveniently in negligibly small computation time.

## CHAPTER 2

### Theoretical Developments

It is possible to make mole balance for various species in the reaction mass and the batch reactor results are given in Table 1. We define concentration of polymer radicals,  $[P]$  as

$$[P] = \sum_{n=1}^{\infty} [P_n] \quad (5)$$

With the help of eqn (1.2) of Table 1, one can derive an expression for the time variation of  $[P]$  as below

$$\frac{d[P]}{dt} = 2fk_d[I_2] - k_t[P]^2 \quad (6)$$

When the gel and thermal effects are present in radical polymerization, the rate constants  $k_I$  and  $k_t$  are dependant on temperature and monomer conversion and therefore cannot be integrated. We will show that eqn (6) has a solution for constant  $k_I$  and  $k_t$  and then develop an analytical solution of isothermal polymerization in absence of gel effect. Subsequently we will show that these results can be naturally adopted in the presence of the gel and thermal effects.

#### Solution of Isothermal Radical Polymerization:

The mole balance for the initiator given in eqn (1.1) of Table 1 can be integrated for time invariant  $fk_d$  as

$$[I_2] = [I_2]_0 e^{-fk_d t} \quad (7)$$

In the above eqn,  $[I_2]_0$  is the concentration of initiator at  $t=0$ .

Let us now transform  $[P]$  in eqn (6)

$$[P] = \frac{1}{k_t} \frac{dy/dt}{y} \quad (8)$$

and upon substituting eqn (7) for  $[I_2]$  in eqn (6) one obtains,

$$\frac{d^2y}{dt^2} = 2fk_d k_t [I_2]_0 e^{-fk_d t} y \quad (9)$$

Further, we define  $x$  related to time of polymerization as

$$x = 2fk_d k_t [I_2]_0 e^{-fk_d t} \quad (10)$$

This gives

$$\frac{dx}{dt} = -fk_d x \quad (a)$$

$$\frac{dy}{dt} = \frac{dy}{dx} \frac{dx}{dt} = -fk_d x \frac{dy}{dx} \quad (b)$$

$$\frac{d^2 y}{dt^2} = \frac{d}{dx} \left( \frac{dy}{dt} \right) \frac{dx}{dt} \quad (c)$$

$$= (fk_d)^2 x \frac{dy}{dx} + (fk_d)^2 x^2 \frac{d^2 y}{dx^2} \quad (d) \quad (11)$$

In terms of these, eqn (9) becomes

$$(fk_d)^2 x^2 \frac{d^2 y}{dx^2} + (fk_d)^2 x \frac{dy}{dx} - xy = 0 \quad (12)$$

we further transform  $x$  by

$$Z = 2\sqrt{bx} \quad (a)$$

$$\text{where } b = \left( \frac{1}{fk_d} \right)^2 \quad (b) \quad (13)$$

in terms of which eqn (12) reduces to

$$Z^2 \frac{d^2 y}{dz^2} + Z \frac{dy}{dz} - (Z^2 - 0) y = 0 \quad (14)$$

For this  $y$  has the following solution

$$y = C_1 I_0(Z) + C_2 K_0(Z) \quad (15)$$

Where  $I_0(Z)$  and  $K_0(Z)$  are the modified zeroth order Bessel functions and  $C_1$  and  $C_2$  are the constants of integration. With the help of eqn (8), one can get  $[P]$  as

$$[P] = - \frac{fk_d Z}{2k_t} \frac{1}{y} \frac{dy}{dz} \quad (16)$$

$$= \frac{fk_d Z}{2k_t} \frac{C_2 K_1(Z) - C_1 I_1(Z)}{C_2 K_0(Z) + C_1 I_0(Z)}$$

$$= \frac{fk_d Z}{2k_t} \frac{K_1(Z) - C I_1(Z)}{K_0(Z) + C I_0(Z)} \quad (17)$$

where  $C = C_1/C_2$ , which is to be determined by the initial conditions

Let us assume that at  $t=0$ , the concentration of Polymer radicals is  $[P]_0$ . In the Z plane, time  $t=0$  corresponds to  $Z_0$  given by

$$Z_0 = 2 \sqrt{\frac{2k_t [I_2]_0}{fk_d}} \quad (18)$$

and C in eqn (17) is given by

$$C = \frac{K_1(Z_0) - \frac{2k_t [P]_0}{fk_d Z_0} K_0(Z_0)}{I_1(Z_0) + \frac{2k_t [P]_0}{fk_d Z_0} I_0(Z_0)}$$

$$\frac{K_1(Z_0)}{I_1(Z_0)} = \frac{[P]_0^* K_0(Z_0)}{I_1(Z_0)} \quad (19)$$

$$\frac{1 + [P]_0^* \frac{I_0(Z_0)}{I_1(Z_0)}}{1 + [P]_0^* \frac{I_0(Z_0)}{I_1(Z_0)}}.$$

where  $[P]_0^* = \frac{[P]_0}{[P]_S} = [P]_0 \sqrt{\frac{k_t}{2fk_d [I_2]_0}} \quad (20)$

Above  $[P]_S$  is the concentration of polymer radicals assuming the steady state approximation and is given by eqn (4)

The variation in the monomer concentration,  $[M]$ , is governed by eqn (1.3) of Table 1. We substitute eqn (13) in it to obtain

$$\frac{d[M]}{dt} = \frac{d[M]}{dz} \frac{dz}{dt} = - \frac{fk_d Z}{2} \frac{d[M]}{dz} = - k_p [M] [P]$$

or

$$\frac{fk_d Z}{2} \frac{d[M]}{dz} = k_p [M] \frac{fk_d Z}{2k_t} \frac{K_1(Z) - C I_1(Z)}{K_0(Z) + C I_0(Z)}$$

$$\frac{d[M]}{dz} = [M] \frac{k_p}{k_t} \left( \frac{K_1(z) - C I_1(z)}{K_0(z) + C I_0(z)} \right) \quad (21)$$

We substitute

$$u = K_0(z) + C I_0(z) \quad (22)$$

which on differentiating with respect to  $Z$  gives

$$\frac{du}{dz} = -K_1(z) + C I_1(z) \quad (23)$$

Comparison of equations (19) and (21) gives

$$\frac{-d[M]}{[M]} \frac{k_p}{k_t} \frac{du}{u} \quad (24)$$

which on integration leads to

$$[M] = [M]_0 \left[ \frac{K_0(z) + C I_0(z)}{K_0(z_0) + C I_0(z_0)} \right]^{-k_p/k_t} \quad (25)$$

Above  $[M]_0$  is the monomer concentration at  $t=0$  (or  $Z=z_0$ ) and  $z_0$  is defined in eqn (18).

The magnitude of  $Z$  as defined in eqn (13) is very large. For example, for methyl methacrylate polymerizing at  $60^\circ\text{C}$  with AIBN  $[I_2]_0 = 0.0258$  moles/lit] initiator, the rate constants  $k_d$ ,  $k_p$  and  $k_t$  are  $0.475 \times 10^{-3} \text{ min}^{-1}$ ,  $0.4117 \times 10^5 \text{ lit/mol min}$  and  $0.20383 \times 10^{10} \text{ lit/mol min}$  respectively. Taking initiator efficiency  $f$  to be 0.58, we get at time  $t=0$ , 'b' as defined in eqn (13) and  $x_0$  defined by eqn (10) to be  $1.3175 \times 10^7$  and  $2.8756 \times 10^4$  respectively. Therefore  $Z$  at time  $t=0$  is given by eqn (18) and is equal to  $0.1231 \times 10^7$ . Hence the asymptotic expansion of Bessel functions valid for large arguments ( $Z > 5$ ) may be used<sup>8</sup>.

Neglecting terms involving  $Z$  in the denominator, we get

$$K_1(z) = K_0(z) = \sqrt{\frac{\pi}{2z}} e^{-z}$$

$$I_1(Z) = I_0(Z) = \frac{e^Z}{\sqrt{2\pi Z}} \quad (26)$$

Making use of the above approximations for Bessel functions, C defined in eqn (19) gives

$$C = \psi \pi e^{-Z_0} \quad \text{where } \psi = \frac{1 - [P]_0^*}{1 + [P]_0^*} \quad (27)$$

The eqn. (17) for [P] may be written as

$$P = \frac{f k_d Z}{2 k_t} \frac{\frac{K_1(Z)}{I_0(Z)} - C \frac{I_1(Z)}{I_0(Z)}}{\frac{K_0(Z)}{I_0(Z)} + C}$$

After substituting for C and Bessel functions, we get an expression for the time variation of [P] as

$$[P] = \frac{f k_d Z}{2 k_t} \frac{1 - \psi e^{-2(Z_0 - Z)}}{1 + \psi e^{-2(Z_0 - Z)}} \quad (28)$$

The quantities  $CI_0(Z)$  and  $CI_0(Z_0)$  in eqn (25) for [M] are given by

$$CI_0(Z) = \psi \pi e^{-Z_0} \frac{e^{-(Z_0 - Z)}}{\sqrt{2\pi Z}} \\ CI_0(Z_0) = \frac{\psi \pi e^{-Z_0}}{\sqrt{2\pi Z_0}} \quad (29)$$

These may be taken as zero, since both  $Z_0$  and Z are of the order  $10^6$ . Hence the eqn (25) for [M] simplifies to

$$[M] = [M]_0 e^{-m(Z_0 - Z)} \quad (30)$$

where  $m = \frac{k_p}{k_t}$

By making use of the above expressions for  $[M]$  and  $[P]$ , we can obtain analytical expressions for various moments of radical and dead polymer distributions.

#### Radical and Dead Polymer Moments:

The differential equation for first moment  $Q_1$  for radical distribution  $\left( = \sum_{n=1}^{\infty} [P_n] \right)$  can be derived from eqn. 1.2 of Table 1 as follows

$$\begin{aligned} \frac{dQ_1}{dt} &= -k_t [P] Q_1 + 2fk_d [I_2] + k_p [M] \{ 2[P_1] + 3[P_2] + 4[P_3] + \dots \} \\ &\quad - k_p [M] \{ [P_1] + 2[P_2] + \dots \} \\ &= -k_t [P] Q_1 + 2fk_d [I_2] + k_p [M] \{ (1[P_1] + 2[P_2] + 3[P_3] + \dots) + \\ &\quad ([P_1] + [P_2] + [P_3] + \dots) \} \\ &\quad - k_p [M] \{ [P_1] + 2[P_2] + 3[P_3] + \dots \} \\ \frac{dQ_1}{dt} &= 2fk_d [I_2] - k_t [P] Q_1 + k_p [M] [P] \end{aligned} \quad (31)$$

The above equation is a linear differential equation of first order if we assume rate constants as time invariant. We get the integrating factor (I.F.) as follows

$$I.F. = \exp \{ k_t \int [P] dt \} \quad (32)$$

Observing that

$$\frac{d \{ [M]/[M]_0 \}}{\{ [M]/[M]_0 \}} = -k_p [P] dt \quad (33)$$

eqn (32) reduces to

$$\begin{aligned} I.F. &= \exp \left\{ -\frac{1}{m} \ln \left( \frac{[M]}{[M]_0} \right) \right\} \\ &= \left\{ \frac{[M]}{[M]_0} \right\}^{-1/m} \end{aligned} \quad (34)$$

The integration of the differential equation (eqn 31) gives  $Q_1$  as

$$Q_1 \left\{ \frac{[M]}{[M]_0} \right\}^{\frac{1}{m}} = \int (2fk_d [I_2] + k_p [M]_0 \left\{ \frac{[M]}{[M]_0} \right\} [P]) \left\{ \frac{[M]}{[M]_0} \right\}^{\frac{1}{m}} dt$$

Substituting  $[I_2]$  from eqn (13) in terms of  $Z$  as

$$[I_2] = \frac{Z^2 fk_d}{8k_t}$$

and carrying out the integration to finally obtain,

$$Q_1 = C_1 \left( \frac{[M]}{[M]_0} \right) + C_2 \left( \frac{[M]}{[M]_0} \right)^{1/m} + \frac{fk_d}{2k_t} (Z_0 + 1) \quad (35)$$

$$\text{where } C_1 = \frac{-[M]_0}{1-17m} \text{ and } C_2 = Q_{10} + \frac{[M]_0}{1-17m} - \frac{fk_d}{2k_t} (Z_0 + 1) \quad (36)$$

In order to derive the differential equations governing zeroth, first and second moments of dead polymer distribution, we make use of the mole balance for  $M_n$  from Table 1. We have

$$\frac{d[M_n]}{dt} = \frac{k_{tc}}{2} \sum_{m=1}^{n-1} [P_m] [P_{n-m}] + k_{td} [P_n] \sum_{n=1}^{\infty} [P_n] \quad (37)$$

Further we know that,

$$\sum_{n=2}^{\infty} n^k \sum_{m=1}^{n-1} [P_m] [P_{n-m}] = \sum_{n=1}^{\infty} [P_n] \sum_{m=1}^{n-1} (m+n)^k [P_m] \quad (38)$$

The zeroth moment of dead polymer distribution  $\lambda_0 = \left( \sum_n M_n \right)$  can

be derived by adding eqn (37) for all  $n$

$$\frac{d\lambda_0}{dt} = \frac{k_{tc}}{2} [P]^2 + k_{td} [P]^2 \quad (39)$$

where  $[P] = \sum_{n=1}^{\infty} [P_n]$  and

eqn (38) is made use of to obtain eqn (39)

Making use of eqn (33)

$$[P] dt = \frac{-1}{k_p} \frac{d([M]/[M]_0)}{[M]/[M]_0}$$

we get,

$$\int d\lambda_0 = \frac{-(0.5k_{tc} + k_{td})}{k_p} \int [P] \frac{d([M]/[M]_0)}{([M]/[M]_0)}$$

From eqn (30).  $\frac{d([M]/[M]_0)}{([M]/[M]_0)} = m dz$

and hence  $\lambda_0 - \lambda_{00} = - \frac{(0.5k_{tc} + k_{td})m}{k_p} \int [P] dz$  (40)

Substituting for  $[P]$  from eqn. (28), we get

$$\lambda_0 - \lambda_{00} = \int d\lambda_0 = -(0.5 k_{tc} + k_{td}) \frac{m}{k_p} \frac{fk_d}{2k_t} \int Z \cdot \frac{1-\psi e^{-2(Z_0-Z)}}{1+\psi e^{-2(Z_0-Z)}} dz \quad (41)$$

The rigorous evaluation of the integral leads to an infinite series and is given in Appendix I. However, if  $Z$  above is assumed to be approximately equal to  $Z_0$ , the integration in eqn (41) is considerably simplified without affecting results very much. On doing so eqn (41) leads to

$$\lambda_0 - \lambda_{00} = \int d\lambda_0 = -(0.5 k_{tc} + k_{td}) \frac{m}{k_p} \frac{fk_d Z_0}{2k_t} \int \frac{1-\psi e^{-2(Z_0-Z)}}{1+\psi e^{-2(Z_0-Z)}} dz \quad (42)$$

This can be easily integrated to

$$\lambda_0 - \lambda_{00} = \frac{(0.5k_{tc} + k_{td})}{4k_p k_t} m fk_d Z_0 \left[ 2(Z_0 - Z) - 2\ln(1+\psi) + 2\ln(1+\psi e^{-2(Z_0-Z)}) \right] \quad (43)$$

The differential equation for first moment  $\left( \lambda_1 = \sum_{n=1}^{\infty} n [M]_n \right)$

of dead polymer distribution is similarly derived using eqns (37) and (38) as follows:

$$\begin{aligned} \frac{d \sum n [M]_n}{dt} &= k_{td} [P] \sum_{n=0}^{\infty} n [P]_n + \frac{k_{tc}}{2} \sum_{n=0}^{\infty} [P]_n \sum_{m=1}^{n-1} (m+n) [P]_m \\ &= k_{td} [P] Q_1 + \frac{k_{tc}}{2} \sum_{n=0}^{\infty} [P]_n (Q_1 + n[P]) \\ &= k_{td} [P] Q_1 + \frac{k_{tc}}{2} \cdot 2Q_1 [P] \end{aligned} \quad (44)$$

On eliminating  $[P]$  with the help of eqn. 1.3 of Table 1,

$$\frac{d\lambda_1}{dt} = -\frac{k_t}{k_p} \frac{Q_1}{\{[M]/[M_0]\}} \frac{d\{[M]/[M_0]\}}{dt}$$

Substituting for  $Q_1$ , and using

$$\frac{d\{[M]/[M_0]\}}{\{[M]/[M_0]\}} = m \, dz$$

We get,

$$\lambda_1 - \lambda_{10} = -\frac{k_t}{k_p} \left[ \int_{1}^{\{[M]/[M_0]\}} \left( C_1 + C_2 \left( \frac{[M]}{[M_0]} \right)^{\frac{1}{m}} - 1 \right) d\left( \frac{[M]}{[M_0]} \right) + \int_{z_0}^z \frac{fk_d}{2k_t} (z+1) \, m \, dz \right]_{t=0}$$

where  $\lambda_{10}$  is the value of  $\lambda_1$  at time  $t=0$  and  $C_1$  and  $C_2$  are as defined in eqn (36)

On integrating, we obtain,

$$\lambda_1 - \lambda_{10} = \frac{k_t}{k_p} \left[ C_1 \left( 1 - \frac{[M]}{[M_0]} \right) + m C_2 \left( 1 - \left( \frac{[M]}{[M_0]} \right)^{\frac{1}{m}} \right) \right] + \frac{fk_d}{2k_t} \left[ \frac{1}{2} \left( z_0^2 - z^2 \right) + (z_0 - z) \right] \quad (45)$$

The expression for second moment of Polymer radical distribution  $Q_2 (= \sum n^2 [P_n])$  is derived making use of eqn (1.2) of Table 1, to obtain

$$\begin{aligned} \frac{dQ_2}{dt} &= -k_t [P] Q_2 + 2fk_d [I_2] + k_p [M] (2^2 [P_1] + 3^2 [P_2] + 4^2 [P_3] + \dots) \\ &\quad - k_p M (2^2 [P_1] + 3^2 [P_2] + 4^2 [P_3] + \dots) \\ &= -k_t [P] Q_2 + 2fk_d [I_2] + k_p [M] (1^2 [P_1] + 2^2 [P_2] + 3^2 [P_3] + \dots) \\ &\quad + (1^2 [P_1] + 2^2 [P_2] + 3^2 [P_3] + \dots) + (2 \cdot 1 [P_1] + 2 \cdot 2 [P_2] + \dots) - k_p [M] Q_2 \\ &= -k_t [P] Q_2 + 2fk_d [I_2] + k_p [M] (2Q_1 + [P]) \end{aligned} \quad (46)$$

This is again a linear differential equation of first order.

As before we get the integrating factor to be equal to  $\left(\frac{[M]}{[M]_0}\right)^{-\frac{1}{m}}$ , and hence

$$Q_2 \left(\frac{[M]}{[M]_0}\right)^{-\frac{1}{m}} = \int \left(\frac{[M]}{[M]_0}\right)^{-\frac{1}{m}} \left[ 2fk_d [I_2] + 2k_p [M]_0 \left(\frac{[M]}{[M]_0}\right) Q_1 + b_p [M]_0 [P] \right] dt + \text{constant}$$

Substituting for  $[I_2]$  and  $Q_1$ , we get

$$Q_2 \left(\frac{[M]}{[M]_0}\right)^{-\frac{1}{m}} = \int 2fk_d \frac{Z^2 fk_d}{8k_t} e^{(Z_0 - Z)} \frac{Z \cdot dZ}{-fk_d Z} + \int 2k_p [M]_0 \left(\frac{[M]}{[M]_0}\right)^{-\frac{1}{m}} \left[ C_1 \left(\frac{[M]}{[M]_0}\right) + C_2 \left(\frac{[M]}{[M]_0}\right)^{\frac{1}{m}} \frac{fk_d}{2k_t} (Z+1) \right] \cdot \frac{Z \cdot dZ}{-fk_d Z} + \int \left(\frac{[M]}{[M]_0}\right)^{-\frac{1}{m}} d \left(\frac{[M]}{[M]_0}\right) + C^* \quad (47)$$

We integrate the above expression assuming  $Z = Z_0$ . The rigorous solution has also been derived and is presented in appendix I and we find that the results derived in the following gives results within 0.01%.

$$Q_2 = \frac{fk_d (Z+1)}{2k_t} - \frac{4k_p [M]_0 C_1}{fk_d Z_0 (2m-1)} \left(\frac{[M]}{[M]_0}\right)^2 - \frac{4k_p [M]_0 C_2}{fk_d Z_0^m} \left(\frac{[M]}{[M]_0}\right)^{1+\frac{1}{m}} - \frac{2k_p [M]_0}{k_t (m-1)} \left(\frac{[M]}{[M]_0}\right) - \frac{2k_p [M]_0}{k_t Z_0^{(m-1)}} \left(\frac{[M]}{[M]_0}\right) - \frac{[M]_0}{1-1/m} \left(\frac{[M]}{[M]_0}\right) + C^* \left(\frac{[M]}{[M]_0}\right)^{\frac{1}{m}} \quad (48)$$

where  $C^*$  is evaluated using the initial condition  $Q_2 = Q_{20}$  at  $t=0$ . Therefore we get

$$C^* = Q_{20} - \frac{fk_d (Z_0+1)}{2k_t} + \frac{4k_p [M]_0 C_1}{fk_d Z_0 (2m-1)} + \frac{4k_p [M]_0 C_2}{fk_d Z_0^m} + \frac{2k_p [M]_0}{k_t (m-1)} + \frac{2k_p [M]_0}{k_t Z_0^{(m-1)}} + \frac{[M]_0}{1-1/m} \quad (49)$$

The differential equation for second moment  $\lambda_2 = \sum n^2 [M_n]$  of

dead polymer distribution is derived using Mole balance relation (eqn 37) and eqn (38) as follows:

$$\begin{aligned}
 \frac{d\lambda_2}{dt} &= k_{td} [P] Q_2 + \frac{k_{tc}}{2} \sum_n^2 \sum_m [P_n] [P_{m-n}] \\
 &= k_{td} [P] Q_2 + \frac{k_{tc}}{2} \sum_n [P_n] \sum_m (m^2 + n^2 + 2nm) [P_n] \\
 &= k_{td} [P] Q_2 + \frac{k_{tc}}{2} ([P] Q_2 + [P] Q_2 + 2Q_1^2) \\
 &= (k_{tc} + k_{td}) [P] Q_2 + k_{tc} Q_1^2
 \end{aligned} \tag{50}$$

We observe that

$$\begin{aligned}
 \int k_{tc} Q_1^2 dt &= \frac{-2k_{tc}}{fk_d} \left[ \left[ C_1^2 \left( \frac{[M]}{[M]_0} \right)^2 + C_2^2 \left( \frac{[M]}{[M]_0} \right)^m + \left( \frac{fk_d}{2k_t} \right)^2 (z^2 + 2z + 1) \right. \right. \\
 &\quad + 2C_1 C_2 \left( \frac{[M]}{[M]_0} \right)^{1+\frac{1}{m}} + C_1 \left( \frac{fk_d}{k_t} \right) \left( \frac{[M]}{[M]_0} \right) (z + 1) \\
 &\quad \left. \left. + C_2 \left( \frac{fk_d}{k_t} \right) (z + 1) \left( \frac{[M]}{[M]_0} \right)^{\frac{1}{m}} \right] \frac{dz}{2} \right]
 \end{aligned} \tag{51}$$

Integrating the above equation assuming  $z = z_0$  in the denominator and taking it out of the integral, we get

$$\begin{aligned}
 \int k_{tc} Q_1^2 dt &= \frac{2k_{tc}}{fk_d} \left[ \frac{C_1^2}{2z_0} \left( 1 - \left( \frac{[M]}{[M]_0} \right)^{2z_0} \right) + \frac{C_2^2}{2z_0} \left( 1 - \left( \frac{[M]}{[M]_0} \right)^m \right) \right. \\
 &\quad + \left( \frac{fk_d}{2k_t} \right)^2 \left[ \frac{1}{2} (z_0^2 - z^2) + 2(z_0 - z) + \ln \left( \frac{z_0}{z} \right) \right] \\
 &\quad + \frac{2C_1 C_2}{(m+1)z_0} \left( 1 - \left( \frac{[M]}{[M]_0} \right)^{1+\frac{1}{m}} \right) + \frac{C_1}{m} \frac{fk_d}{k_t} \left( 1 - \left( \frac{[M]}{[M]_0} \right)^{\frac{1}{m}} \right) \\
 &\quad \left. + \frac{C_1}{mz_0} \left( \frac{fk_d}{k_t} \right) \left( 1 - \left( \frac{[M]}{[M]_0} \right)^{\frac{1}{m}} \right) + \frac{C_2 fk_d}{k_t} \left( 1 - \left( \frac{[M]}{[M]_0} \right)^{\frac{1}{m}} \right) \right. \\
 &\quad \left. + \frac{C_2 fk_d}{k_t z_0} \left( 1 - \left( \frac{[M]}{[M]_0} \right)^{\frac{1}{m}} \right) \right]
 \end{aligned} \tag{52}$$

Also,

$$\int k_t [P] Q_2 dt = \frac{-k_t}{k_p} \int \frac{Q_2}{\left[ \frac{[M]}{[M]_0} \right]} d\left[ \frac{[M]}{[M]_0} \right]$$

Substituting  $Q_2$  from eqn (48) and carrying out the integration assuming  $Z = Z_0$  in the denominator we get

$$\begin{aligned} \int k_t [P] Q_2 dt &= \frac{k_t}{k_p} \left[ \frac{mfk_d}{2k_t} \left[ \frac{1}{2} (Z_0^2 - Z^2) + (Z_0 - Z) \right] - \frac{2k_p [M]_0 C_1}{fk_d Z_0 (2m - 1)} \left( 1 - \left[ \frac{[M]}{[M]_0} \right]^2 \right) \right. \\ &\quad \left. - \frac{4k_p [M]_0 C_2}{fk_d Z_0 (m + 1)} \left( 1 - \left[ \frac{[M]}{[M]_0} \right]^{1+\frac{1}{m}} \right) - \frac{2k_p [M]_0}{k_t (m-1)} \left( 1 - \left[ \frac{[M]}{[M]_0} \right] \right) \right. \\ &\quad \left. - \frac{2k_p [M]_0}{k_t Z_0 (m-1)} \left( 1 - \left[ \frac{[M]}{[M]_0} \right] \right) - \frac{[M]_0}{1 - \frac{1}{m}} \left( 1 - \left[ \frac{[M]}{[M]_0} \right] \right) \right. \\ &\quad \left. + mC^* \left( 1 - \left[ \frac{[M]}{[M]_0} \right]^{\frac{1}{m}} \right) \right] \end{aligned} \quad (53)$$

where  $C^*$  is as defined in eqn (49)

Therefore

$$\begin{aligned} \lambda_2 - \lambda_{20} &= \frac{2k_t c}{fk_d} \left[ \frac{c_1^2}{2mZ_0} \left( 1 - \left[ \frac{[M]}{[M]_0} \right]^2 \right) + \frac{c_2^2}{2Z_0} \left( 1 - \left[ \frac{[M]}{[M]_0} \right]^{\frac{2}{m}} \right) \right. \\ &\quad \left. + \left( \frac{fk_d}{2k_t} \right)^2 \left[ \frac{1}{2} (Z_0^2 - Z^2) + 2(Z_0 - Z) + \ln \left( \frac{Z_0}{Z} \right) \right] \right. \\ &\quad \left. + \frac{2c_1 c_2}{(m+1)Z_0} \left( 1 - \left[ \frac{[M]}{[M]_0} \right]^{1+\frac{1}{m}} \right) + \frac{c_1}{m} \frac{fk_d}{k_t} \left( 1 - \left[ \frac{[M]}{[M]_0} \right] \right) \right. \\ &\quad \left. + \frac{c_1}{mZ_0} \left( \frac{fk_d}{k_t} \right) \left( 1 - \left[ \frac{[M]}{[M]_0} \right] \right) + \frac{c_2 fk_d}{k_t} \left( 1 - \left[ \frac{[M]}{[M]_0} \right]^{\frac{1}{m}} \right) \right] \end{aligned}$$

$$\begin{aligned}
& + \frac{C_2 f k_d}{k_t z_0} \left( 1 - \left( \frac{[M]}{[M]_0} \right)^{\frac{1}{m}} \right) \\
& + \frac{k_t}{k_p} \left[ \frac{m f k_d}{2 k_t} \left[ \frac{1}{2} (z_0^2 - z^2) + (z_0 - z) \right] - \frac{2 k_p [M]_0 C_1}{f k_d z_0 (2m - 1)} \left( 1 - \left( \frac{[M]}{[M]_0} \right)^2 \right) \right. \\
& \quad \left. - \frac{4 k_p [M]_0 C_2}{f k_d z_0 (m + 1)} \left( 1 - \left( \frac{[M]}{[M]_0} \right)^{1+\frac{1}{m}} \right) - \frac{2 k_p [M]_0}{k_t (m-1)} \left( 1 - \left( \frac{M}{M_0} \right) \right) \right. \\
& \quad \left. - \frac{2 k_p [M]_0}{k_t z_0 (m-1)} \left( 1 - \left( \frac{[M]}{[M]_0} \right) \right) - \frac{[M]_0}{1 - \frac{1}{m}} \left( 1 - \frac{[M]}{[M]_0} \right) \right. \\
& \quad \left. + m C^* \left( 1 - \left( \frac{[M]}{[M]_0} \right)^{\frac{1}{m}} \right) \right] \quad (54)
\end{aligned}$$

## CHAPTER 3

### Computational Techniques

We have derived the analytical solution for isothermal radical polymerization in batch reactors. In order to check the consistency of these results, we have computed the various reactor parameters using 4th order Runge Kutta numerical technique and checked our results against the analytical solution.

The flow chart of the fourth order Runge Kutta technique is given in Figure 1 and we have varied  $\Delta t$  in Table 4 and seen its effect upon the numerical solution. For stable solution, we find that the time increment  $\Delta t$  must be about 0.0001 min. The flow chart of computation for our analytical solution is given in Fig.2. It must be observed that our analytical solution are given in terms of Z variable. For isothermal reactor there is a straight forward exponential relation. However for nonisothermal cases, there is an ambiguity in terms of properly defining Z. This arises because in general, the rate constants vary with time of polymerization. To overcome this difficulty we recall that in the Runge Kutta technique, the total time of polymerisation is divided into small incremental time. The concentration parameters,  $[M]$ ,  $\lambda_0$ ,  $\lambda_1$ ,  $\lambda_2$ ,  $[P]$ ,  $Q_1$  and  $Q_2$  for the next incremental time are calculated using their values at a given time. This fact has been shown in fig.1. In such computations, between the incremental time the reaction parameters are assumed to be time invariant.

For the cases when the temperature of polymerisation as well as gelation, we similarly divide the total time of

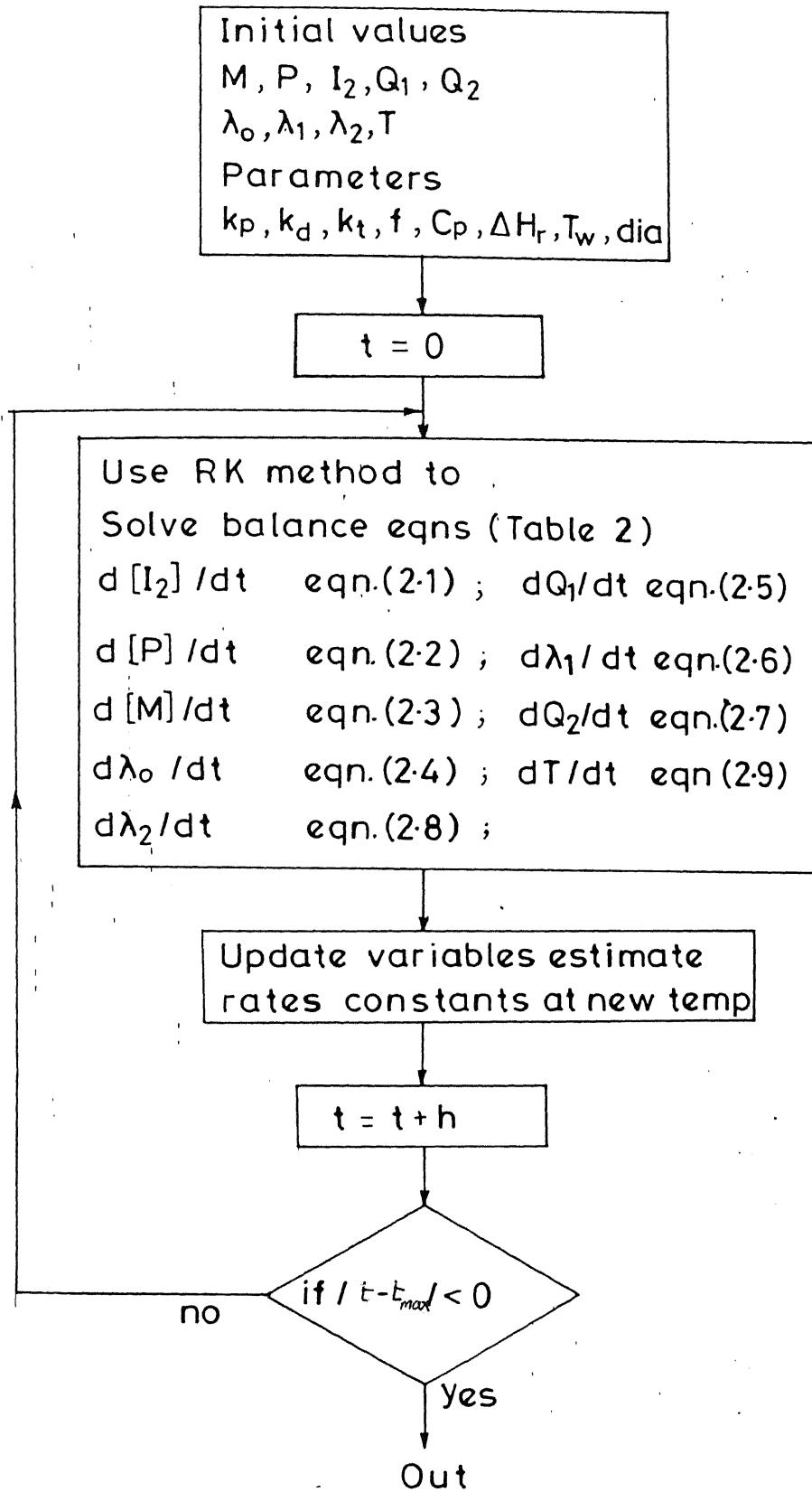


Fig.1 Runge Kutta Scheme for free radical polymerisation

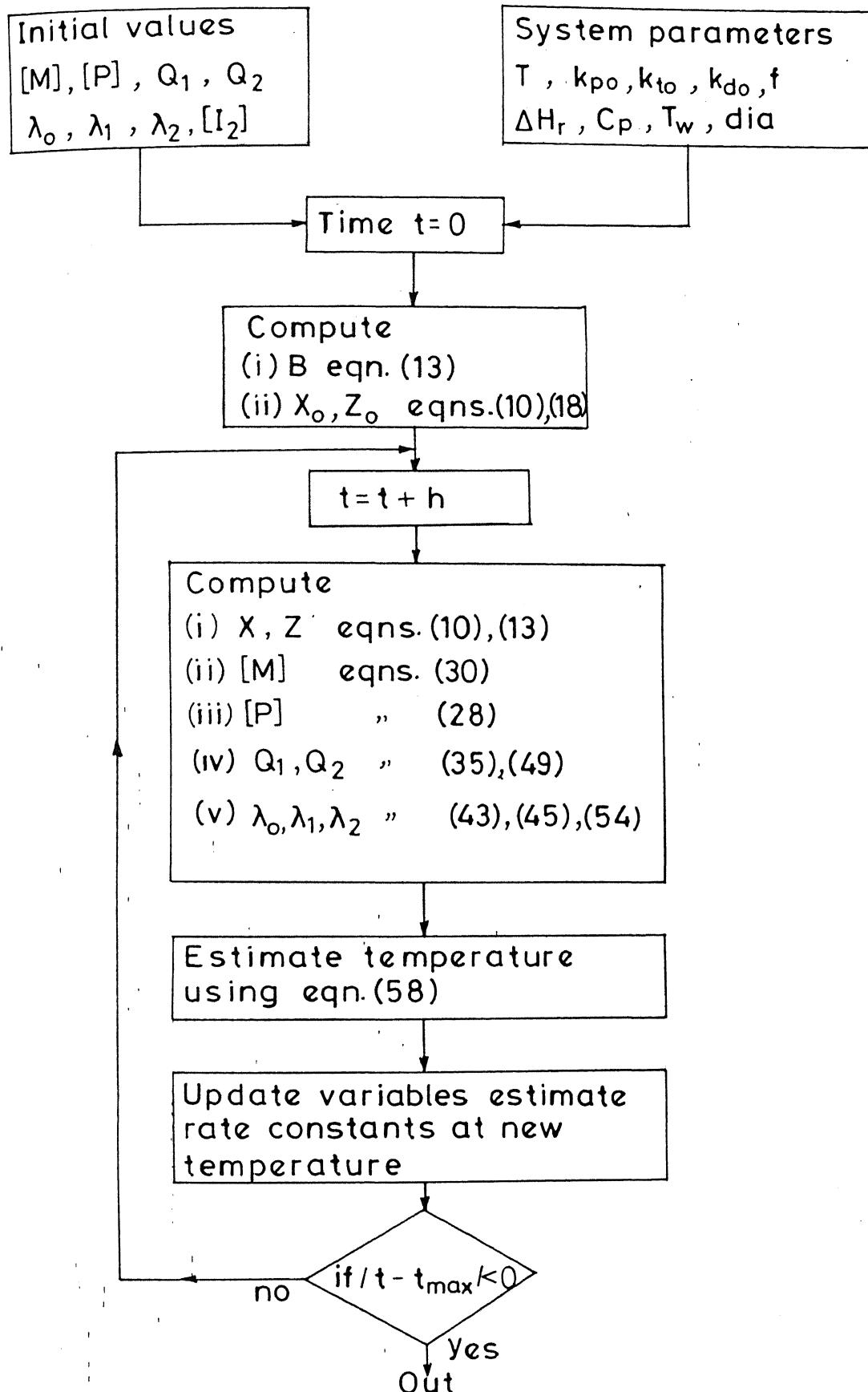


Fig.2 Analytical scheme for free radical polymerisation

polymerization into small incremental times. Between these time increments, we assume that the rate constants are time invariant. If we assume this all the results for isothermal reactors are valid, between the incremental time and only the energy balance equation remains to be integrated, which we do now.

The modelling of nonisothermal polymerization can be done by inclusion of the following energy balance,

$$\rho C_p \frac{dT}{dt} = (-\Delta H_r) k_p [M] [P] - \frac{4U}{D} (T - T_w) \quad (55)$$

Here,  $(-\Delta H_r)$  is the heat of the reaction,  $U$  is the heat transfer coefficient and  $T_w$  is the surrounding temperature.

The above eqn. may be rearranged using eqns. (1-3) and (30) and may be written as follows;

$$\frac{dy}{dx} + \beta y = \alpha e^{-mx} \quad (56)$$

where  $y = T - T_w$  (a)

$$x = Z_o - Z \quad (b)$$

$$\beta = \frac{8U}{D\rho C_p f k_d Z_o} \quad (c)$$

$$\alpha = \frac{(-\Delta H_r) [M]_o \cdot m}{\rho C_p} \quad (d) \quad (57)$$

The integrating factor of eqn.(56) is  $e^{\beta x}$  and using the initial condition  $T=T_o$  at  $x=0$ , we obtain the following solution.

$$T - T_w = \frac{\alpha e^{-m(Z_o - Z)}}{(\beta - m)} + (T_o - T_w) e^{-\beta(Z_o - Z)} - \frac{\alpha e^{-\beta(Z_o - Z)}}{(\beta - m)} \quad (58)$$

This result has been built in the algorithm in figure 2.

## CHAPTER 4

### EXPERIMENTAL

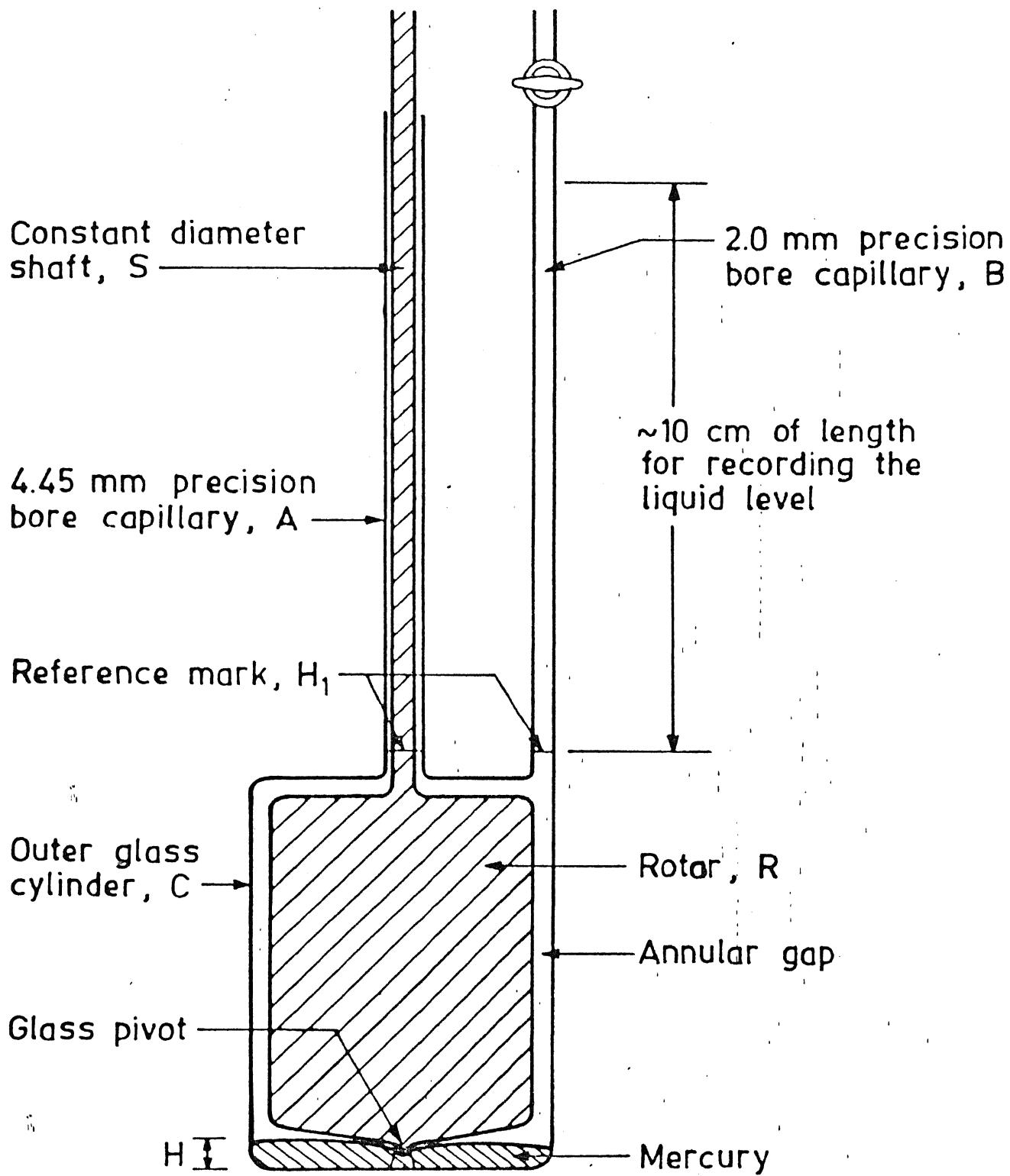
#### (a) Chemicals:

Analytical grade styrene (Burgoyne Burbidge & Co.) is washed with 1.0N NaOH two to three times to remove the inhibitor hydroquinone. In order to remove traces of NaOH left behind, styrene is washed thoroughly with distilled water. The washed styrene is stored over anhydrous calcium chloride atleast for two days in a defreezer, before it is used for our experiments.

The initiator used is 2-2'azo isobutyronitrile and was obtained from SAS chemicals & Co., Bombay. For further purification, it was dissolved in methanol and recrystallised before use. The activated carbon obtained from S.D. fine chemicals, was subjected to dry grinding to obtain various size ranges. Particles of size range -250 mesh and -350 mesh were used.

#### Dilatometer:

A sketch of special dilatometer which combines the features of an ordinary dilatometer and rheometer is shown in figure 3. The instrument consists of a glass cylinder C (I.D. 48.6 mm) having a precision bore capillary A (4.45 mm) exactly at the centre of the cylinder. A stainless steel rod of uniform thickness (o.d. 3.9 mm) passes through the capillary A and connects the rotor R (o. d. 42.5 mm) to a suitable motor. The rotor rests on a glass pivot which facilitates an easy rotation of the rotor. The precision bore capillary B (I.D. 2.0 mm) attached on the side of the cylinder C is used for filling the monomer solution in the annular space. The calibration of the dilatometer has already been done<sup>4</sup>.



For exact measurements, the volume of the dilatometer has to be determined at the temperature at which polymerization is to be carried out (i.e. at  $60^{\circ}\text{C}$ ). However, since the coefficient of linear expansion of glass is more than 2 orders of magnitude smaller<sup>(49)</sup> than the coefficient of cubic expansion of the liquid to be used, the change of the volume of the dilatometer with temperature can generally be neglected.

#### Procedures:

The monomer is taken in a flask and nitrogen is bubbled through it for about 3 minutes. Vacuum is applied to remove any residual nitrogen. This way we ensure that no dissolved oxygen is present in the reaction mass. The dilatometer is filled with mercury upto height  $H$  so that the reaction mixture fills only in the annular space between the rotor, and the glass vessel. The reaction mixture consisting of monomer, activated carbon and initiator with known concentration is charged to the dilatometer upto reference mark  $H_1$  as shown in fig.3. The dilatometer is subsequently placed in a constant temperature bath which is maintained at  $60^{\circ}\text{C}$ . Immediately, the levels of the liquid in the capillaries A and B begin to rise due to the expansion of the liquid but subsequently it falls because of polymerization. The change in liquid level with time in both the capillaries A and B were measured using a cathetometer. The change in volume of the reaction mixture with time is calculated. The rotor R can be rotated at a constant speed by a suitable motor. The speed of rotation is measured by a stroboscope and is maintained at a constant value by carefully monitoring it. After polymerization, the dilatometer is emptied in the following manner. The

dilatometer is inclined carefully over a small beaker so that the mercury can run off, which is then washed with benzene and acetone and finally dried.

The rate of polymerization is calculated by standard dilatometric techniques<sup>1</sup>. The shear rate is calculated using the rheometric equation,

$$\dot{\gamma} = \frac{\omega R_R}{R_G - R_R} \quad (59)$$

where,  $\omega$  is the angular velocity of rotor,  $R_R$  and  $R_G$  are radii of rotor and cylinder respectively.

The dilatometric equation is

$$y = \frac{\rho_{Ps} \times \rho_m}{\rho_{Ps} - \rho_m} \frac{b}{M_w} \frac{1}{V} \frac{1}{[M][I_2]^{1/2}} \quad (60)$$

where,  $\rho_{Ps}$  and  $\rho_m$  are densities of polymer in solution and monomer respectively.  $M_w$  is the molecular weight of monomer,  $V$  is the volume used,  $[M]$  and  $[I_2]$  are the concentration of monomer and initiator respectively.

The experiment is conducted for different concentration of activated carbon and also for different size range of activated carbon.

## CHAPTER 5

### Results and Discussion

The earlier works of Kumar<sup>3</sup> and Shukla<sup>4</sup> have shown that the changes observed in the rate of polymerization,  $r_p$  of styrene-benzoyl peroxide system with shear,  $\dot{\gamma}$  is purely due to variation of initiator efficiency.

The polymerization of styrene has been carried out in a special dilatometer as previously described. The change in height in the capillaries has been measured and converted into the change in volume of the reaction mass. Regressional analysis of experimental runs has been carried out and slopes of  $\Delta V$  versus time plot are used to calculate the rate of polymerization  $r_p$ . The parameter  $y$  as defined in eqn (3) has been calculated and results have been summarized in Tables 7,8,9 and 10.

We have carried out polymerization of styrene under following conditions:

- (1) Polymerization of styrene with AIBN initiator in the absence of activated carbon. and in presence of shear.
- (2) Polymerization of styrene with AIBN initiator in presence of activated carbon (100 mg/200 ml styrene). and in presence of shear.
- (3) Polymerization of styrene-AIBN system in presence of different particle sizes of activated carbon. in absence of shear.

In order to study the effect of shear on rate of polymerization, parameter  $y$  has been defined, which is independent of monomer and initiator concentration. This has been plotted in fig.4. From theoretical considerations, we should have  $y$  independent of shear rate. Contrary to this, we find that with increase in shear rate  $y$  first goes down and then

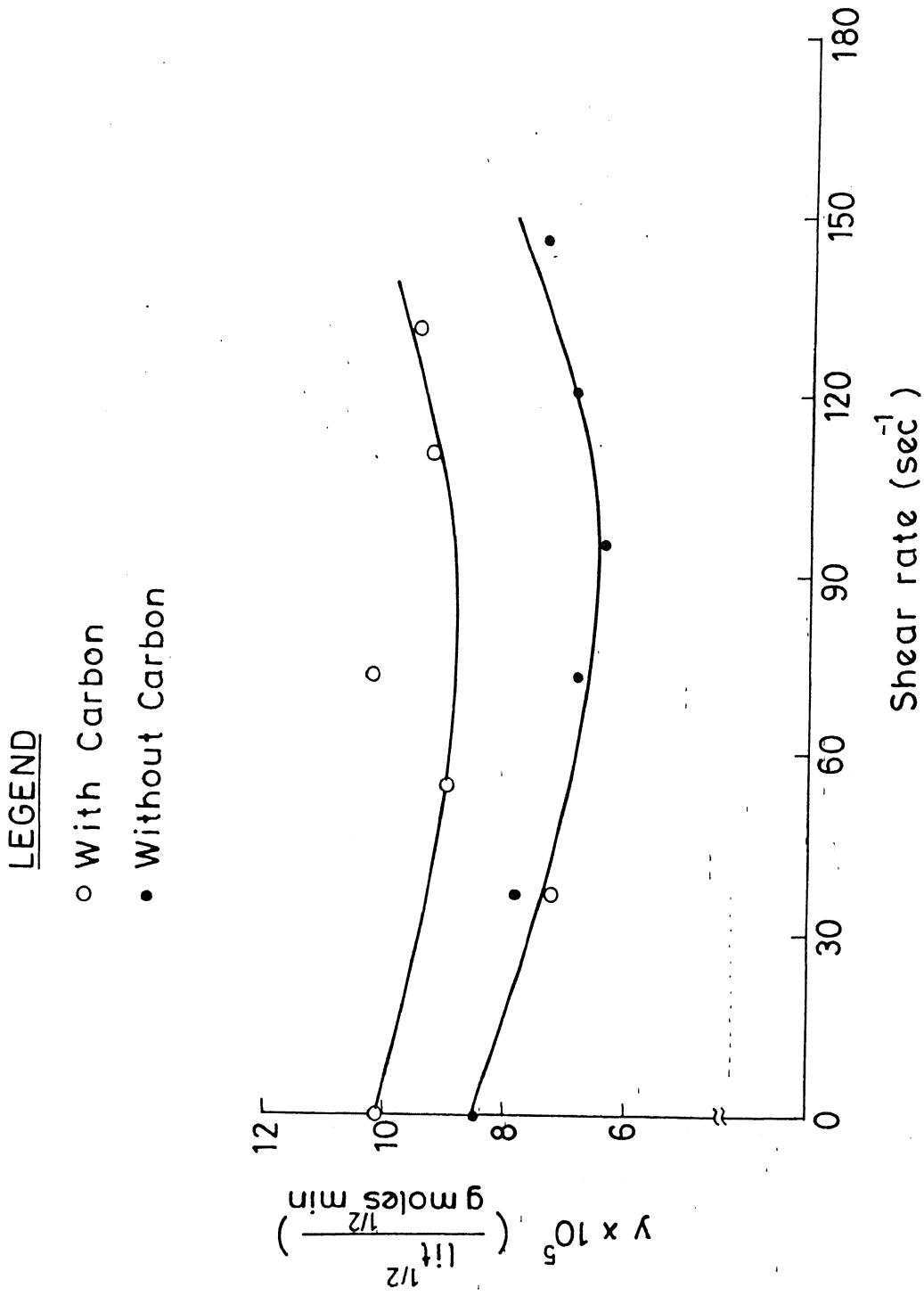
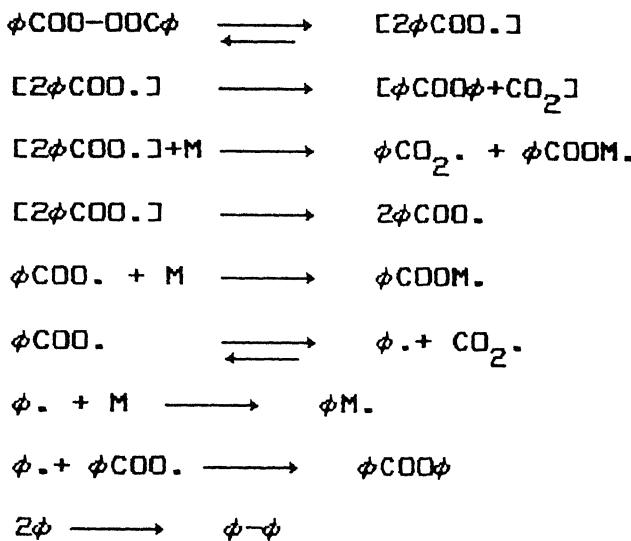


Fig. 4 Variation of  $\gamma$  with shear rate for Styrene AIBN system

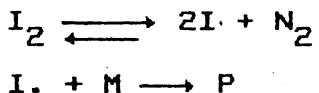
increases to about 95% of its initial value. We have conducted experiments to show that it is the initiator efficiency which is affected by shear.

The most general kinetic model for the cage effect has been discussed by Shukla<sup>4</sup> and is given below:

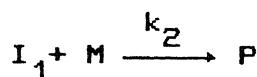
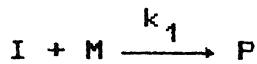
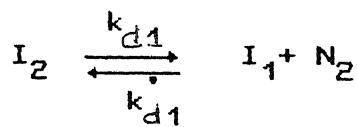
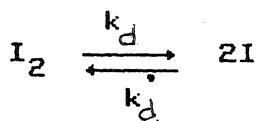


The square bracket indicates the presence of cage and  $\phi$  represents phenyl groups formed in the decomposition of benzoyl peroxide initiator. Instead of considering this detailed model, we simplify and consider the following three idealization in the initiation step.

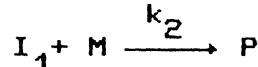
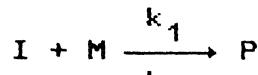
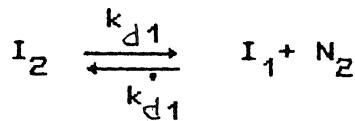
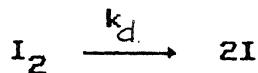
- (1) The initiator decomposes reversibly in the cage to give initiator radicals and  $\text{N}_2$  and the radicals add on to monomer to give polymer radicals.



- (2) The initiator decomposes reversibly to give primary radicals from which  $\text{N}_2$  is eliminated subsequently and both primary and secondary radicals add on to monomer to generate polymer radicals.



(3) The same sequence of steps as above is assumed, the only difference being that the initiator decomposition is assumed to be irreversible.



In appendix 2, these kinetic schemes have been considered and analytical expressions for the rate of polymerization have been derived. If we assume that the reactivities of monomer with primary radicals are comparable to  $k_p$  and those of  $k_{d1}$  and  $k_{d1}'$  are comparable to  $k_d$  and  $k_d'$ , it can then be shown that there is negligible effect of  $N_2$  concentration upon  $f$ . This suggests that models on cage effect alone are unable to explain the phenomenon experimentally observed. The fall in the rate of polymerization (and a subsequent rise) suggests that the  $N_2$  gas dissolved in the reaction mass must be acting as a catalyst on the formation of primary radicals as follows:



The rate of polymerization can then be derived as

$$r_p = k_p \left\{ \frac{fk_d [N_2][I_2]}{k_t} \right\}^{1/2} [M]$$

On the application of shear the concentration of  $N_2$  falls due to enhanced mass transfer. As a result the rate of polymerization falls as shown by above equation. However, for large shear, the cages present initially are destroyed and the initiator efficiency recovers as has been observed experimentally.

We have carried out experiments in presence of activated carbon and we find that the rate of polymerization is increased in its presence. We notice that the activated carbon, has a distribution of particle size and we decided to separate them into -350 and -250 mesh screens. Subsequently we activated them by putting them in oven for 4 hours. In figure 5, we find that the smaller the particle size the larger is the rate of reaction and hence  $y_0$  value. We also examined the polymerization of styrene in presence of carbon as well as the shear rate. When shear is applied the rate of polymerization falls down. In presence of carbon, when shear is applied a similar behaviour is observed except that rate of polymerization is higher in presence of carbon at a given shear rate.

There have been several studies involving activated carbon in the past and these studies focussed on fixing styrene polymer chain to carbon particles. The affixing of styrene chain on carbon particles can occur only when carbon particle was participating in the process of polymerization. Based upon the this we propose that when a given carbon particle is bombarded

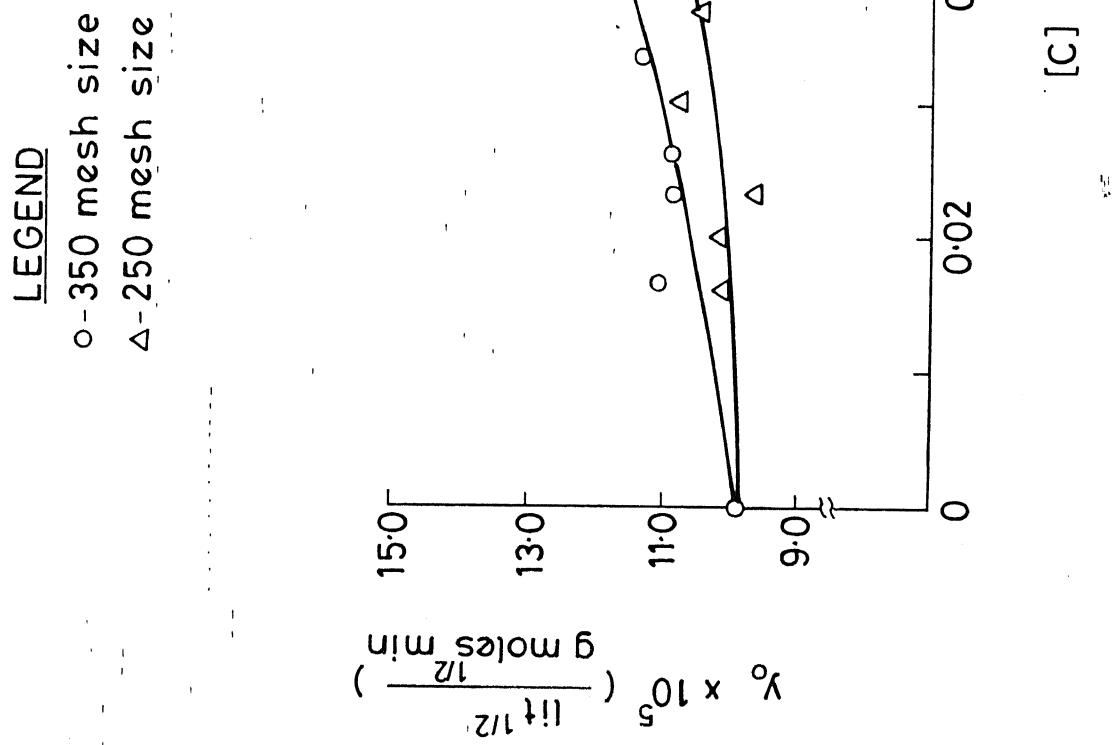
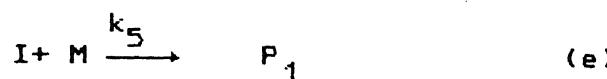
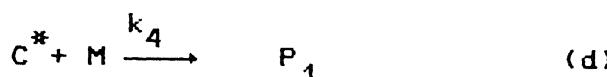
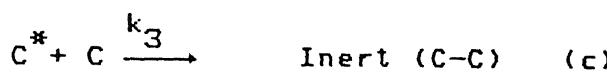
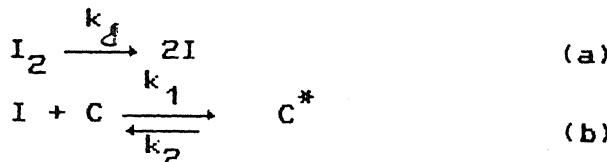


Fig. 5 Variation of  $Y_0$  with activated Carbon Concentration for Styrene AIBN-system

with an initiator radical it forms some kind of an activated species  $[C^*]$ . We propose that this activated species can react with another carbon to form an inert molecule or can react with a monomer to give a grafted polymer molecule. In presence of carbon, the mechanism of polymerization can then be written as

Initiation:



Propagation



Termination



The derivation of rate of polymerization in presence of carbon has been given in appendix 3, and the following expression has been derived.

$$\frac{1}{r_p - r_{p0}} = \frac{K_1^*}{[C]I} + K_2^* \quad (62)$$

where  $K_1^*$  and  $K_2^*$  are constants dependent on temperature, monomer and initiator concentration as follows

$$K_1^* = \frac{k_2 + k_4[M]}{\frac{k_1 k_4 k_d}{k_5}} \quad (a)$$

$$K_2^* = \frac{k_3}{\frac{k_1 k_4 k_d}{k_5} [I_2]_{CM}} \quad (b) \quad (63)$$

For the two particle size activated carbon, we have carried this exercise in Fig.6. We find that we can well represent the data by straight-line according to eqn.(62) and the constants  $K_1^*$  and  $K_2^*$  are different for different particle sizes.

We have considered the batch reactor simulation of radical polymerization. The basic differential equations governing this are given in Table 2. The numerical integration of radical polymerization is difficult for the following reason. It may be recalled that the molar concentration of intermediate polymer radicals is of the order of  $10^{-8}$ . As opposed to this the monomer concentration is of the order of 10 while the reactor temperature is of the order of  $10^2$ . Due to wide variation in the ranges of various reactor parameters, the differential equations of Table 2 are numerically 'stiff' in nature and require selection of very small time increment  $\Delta t$ . In order to remove this numerical stiffness, we have attempted in this thesis, to determine an analytical solution of radical polymerization in batch reactors.

We have assumed the reactor to be isothermal and transformed the mole balance of polymer radicals into Z domain and have successfully obtained the analytical result. Since the value of Z is very large it was possible to develop an approximation in eqn.(28). The testing of this relation with those of Runge-Kutta numerical result are given in Table 5 and is seen that both results are almost identical for the entire range.

For nonisothermal case, we divide the total time of

LEGEND

○ - 350 mesh size

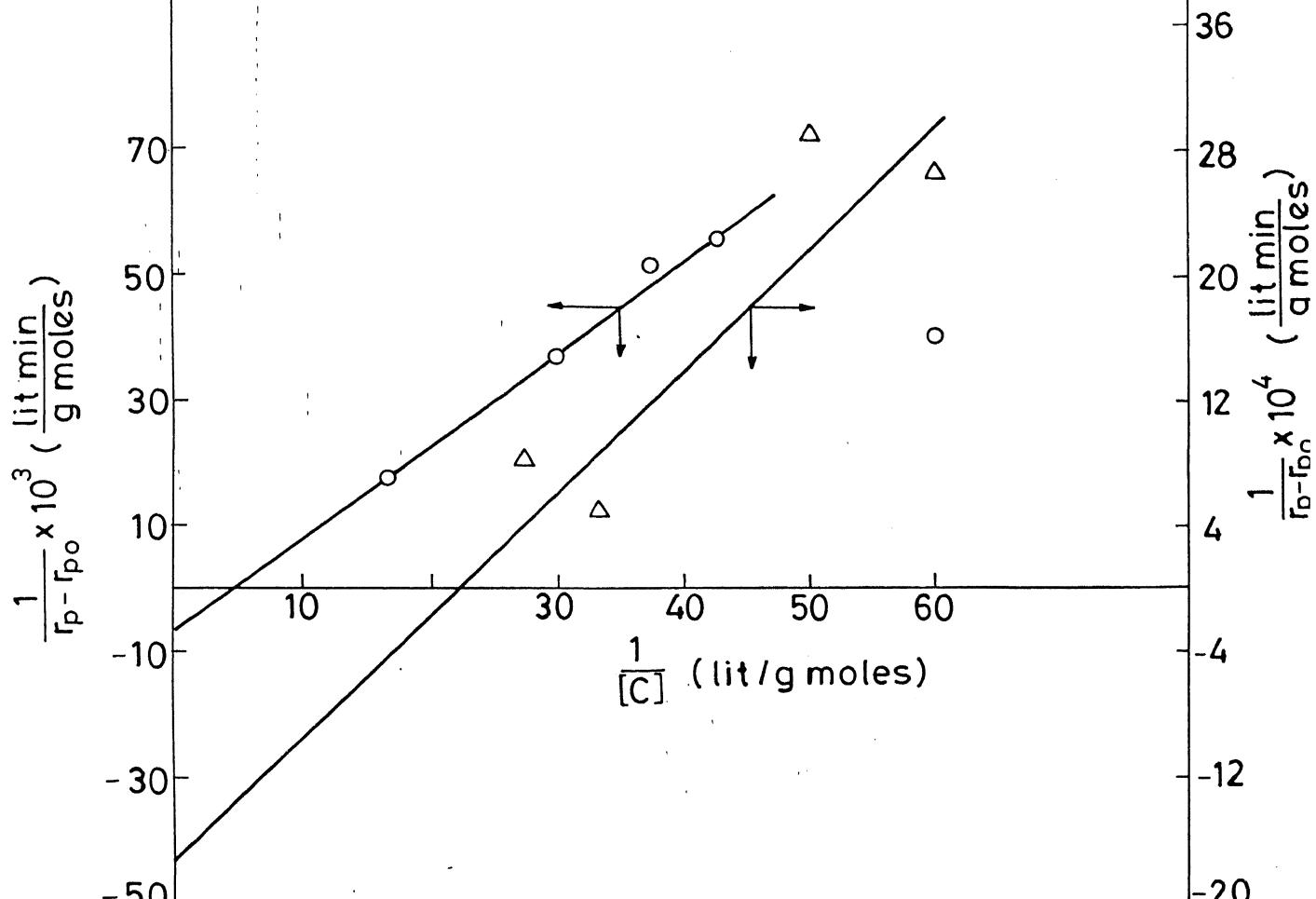
$$K_1^* = 1.54 \times 10^{-3} \text{ min}^{-1}$$

$$K_2^* = 7.0 \times 10^{-3} \frac{\text{lit min}}{\text{g moles}}$$

△ - 250 mesh size

$$K_1^* = 0.9 \times 10^{-4} \text{ min}^{-1}$$

$$K_2^* = 1.75 \times 10^{-3} \frac{\text{lit min}}{\text{g moles}}$$

Fig. 6 Plot of  $\frac{1}{r_p - r_{p0}}$  versus  $\frac{1}{[C]}$

polymerization into small incremental time. Between this incremental time we assume the reactor performance as isothermal and use the analytical solution of the reactor developed so far. The integration of the energy equation has been done in eqn.(58) and the algorithm has been described in figure 2. With this algorithm, the results have been computed and summarized in Table 6. In the same Table the numerical results obtained from Runge-Kutta technique are also given. We find on comparison that both results are close to within 1% in the entire time range.

## CHAPTER 6

### CONCLUSIONS

In this work, we have studied the effect of shear on the rate of polymerization of styrene. It was observed that  $r_p$  decreases on application of shear and then partly recovers. We have considered several models of initiator efficiency and on careful examination we find that none of these can explain the experimental observation in the entire range. It is then suggested that  $N_2$  evolved in the decomposition of initiator has a catalytic effect on the addition of monomeric units. The application of shear helps removal of  $N_2$  from the reaction mass with a consequent fall in  $r_p$ . At high shear rate there is a likelihood that the evolved  $N_2$  is unable to disengage from the reaction mass. As a consequence the rate of polymerization goes up due to higher concentration of  $N_2$  in the reaction mass. From the past studies, it is known that in presence of activated carbon, the latter participates in the initiation step of polymerization. We have consequently developed a kinetic model in which carbon participates in the polymerization. The model suggests that the specific surface area of carbon is important, which would in turn mean that small particle size of carbon would give higher activity. We separated commercially available activated carbon into -250 and -350 mesh particles and we find that the latter exhibits higher activity, this way confirming the proposed kinetic model.

Simulation of free radical polymerization has also been carried out. The nonlinear differential equation for  $[P]$  has been reduced to a form which has its solution in terms of Bessel function, by a suitable transformation. Analytical expressions have been derived for various moments for the case of isothermal polymerization and this has been adopted for nonisothermal polymerization in presence of gel effect.

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## Appendix I

### Rigorous Solution of Dead Polymer and Radical Moments

We have assumed that  $Z = Z_0$  in eqns. (41) (47) and (52) in the derivation of equations for  $\lambda_0$ ,  $Q_2$  and  $\lambda_2$ . The rigorous solution for the above distributions, is given here.

We find that in the derivation of the equations for dead polymer and polymer radical distributions, the integral,

$$I = \int \frac{e^{-a(Z_0-Z)}}{Z} dZ \quad (A 1.1)$$

arises naturally.

Making use of the transformation  $Z_0 - Z = u$ , we can write

$$\begin{aligned} I &= - \int \frac{e^{-au}}{(Z_0-u)} du \\ &= - \frac{1}{Z_0} \left[ \sum_{n=0}^{\infty} \frac{1}{Z_0^n} \int u^n e^{-au} du \right] \quad (A 1.2) \end{aligned}$$

Since

$$\int u^n e^{au} du = e^{au} \sum_{r=0}^n \frac{(-1)^r n! u^{n-r}}{(n-r)! a^{r+1}} \quad (A 1.3)$$

we get the integral as

$$I = e^{-a(Z_0-Z)} \sum_{r=0}^n \frac{1}{Z_0^{n+1}} \sum_{r=0}^n \frac{n! (Z_0-Z)^{n-r}}{(n-r)! a^{r+1}} \quad (A 1.4)$$

The zeroth moment  $\lambda_0$  is therefore given by

$$\int d\lambda_0 = - \frac{(0.5k_{tc} + k_{td}) m f k_d}{2 k_p k_t} \int Z \frac{1-\psi}{1+\psi} \frac{e^{-2(Z_0-Z)}}{e^{-2(Z_0-Z)}} dZ + \text{Const}$$

We can write

$$\int z \frac{1-\psi}{1+\psi} \frac{e^{-2(z_0-z)}}{e^{-2(z_0-z)}} dz = -z_0 \int \frac{1-\psi}{1+\psi} \frac{e^{-2(z_0-z)}}{e^{-2(z_0-z)}} d(z_0-z) \\ + \int (z_0-z) \frac{1-\psi}{1+\psi} \frac{e^{-2(z_0-z)}}{e^{-2(z_0-z)}} d(z_0-z)$$

consider the integral,

$$\int (z_0-z) \frac{1-\psi}{1+\psi} \frac{e^{-2(z_0-z)}}{e^{-2(z_0-z)}} d(z_0-z) \\ = \int x \frac{1-\psi}{1+\psi} \frac{e^{-2x}}{e^{-2x}} dx$$

This can be integrated by parts by assuming

$$v = \int \frac{1-\psi}{1+\psi} \frac{e^{-2x}}{e^{-2x}} dx \\ = \int \left( 1 - \frac{2\psi}{1+\psi} \frac{e^{-2x}}{e^{-2x}} \right) dx \\ v = x + \ln \left[ 1 + \psi e^{-2x} \right] \quad (A 1.5) \\ \int v du = \int \left[ x + \ln \left[ 1 + \psi e^{-2x} \right] \right] dx$$

However, we know that

$$\int \frac{\ln(a+bx)}{x} dx$$

cannot be expressed as a finite combination of elementary functions<sup>7</sup>. Therefore we express the term involving logarithmic function as a series

$$\therefore \ln(1+Y) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{Y^n}{n}$$

where  $Y = \psi e^{-2x}$

Therefore

$$\begin{aligned} \int v du &= \frac{x^2}{2} + \int \left( \psi e^{-2x} - \frac{\psi^2 e^{-4x}}{2} + \frac{\psi^3 e^{-6x}}{3} - \dots \right) dx \\ &= \frac{x^2}{2} + \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n e^{-2nx}}{2n^2} \end{aligned} \quad (A 1.6)$$

Hence we get

$$\int x \frac{1-\psi e^{-2x}}{1+\psi e^{-2x}} dx = \frac{x^2}{2} + x \ln(1+\psi e^{-2x}) - \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n e^{-2nx}}{2n^2} \quad (A 1.7)$$

It is also seen that

$$\begin{aligned} -Z_0 \int \frac{1-\psi e^{-2(Z_0-Z)}}{1+\psi e^{-2(Z_0-Z)}} d(Z_0-Z) &= -Z_0 v \\ &= -Z_0 \left( x + \ln(1 + \psi e^{-2x}) \right) \end{aligned} \quad (A 1.8)$$

writing

$$\Delta = (0.5k_{tc} + k_{td}) \frac{m f k_d}{2 k_p k_t}$$

we have

$$\lambda_0 = \Delta \left[ \frac{1}{2} (Z_0^2 - Z^2) + Z \ln(1 + \psi e^{-2(Z_0-Z)}) + \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n e^{-2n(Z_0-Z)}}{2n^2} \right] + C_1 \quad (A 1.9)$$

where  $C_1$  is the constant of integration to be evaluated using the initial condition,  $\lambda_0 = \lambda_{00}$  at  $t=0$  (or  $Z = Z_0$ )

We get,

$$C_1 = \lambda_{00} - \Delta \left[ Z_0 \ln(1 + \psi) + \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n}{2n^2} \right]$$

Hence we finally obtain

$$\lambda_0 - \lambda_{00} = \Delta \left[ \frac{1}{2} (Z_0^2 - Z^2) + \ln \left\{ \frac{(1+\psi e^{-2(Z_0-Z)})}{(1+\psi)^{Z_0}} \right\} - \sum_{n=1}^{\infty} \frac{(-1)^n \psi^n}{2n^2} (1 - e^{-2n(Z_0-Z)}) \right] \quad (A 1.10)$$

The equation for second moment of polymer radical distribution (from Eqn (46)) is

$$Q_2 \left( \frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} = \int \left( \frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} \left[ 2fk_d [I_2] + 2k_p [M] Q_1 + k_p [M] [P] \right] dt$$

This can be split into three integrals, as

$$Q_2 \left( \frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} = \int 2fk_d [I_2] \left( \frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} dt + \int 2k_p [M] Q_1 \left( \frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} dt + \int \left( \frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} k_p [M] [P] dt$$

(A 1.11)

The first integral  $I_1$  gives

$$I_1 = \frac{fk_d}{2k_t} (Z + 1) \quad (A 1.12)$$

The second integral  $I_2$  is

$$I_2 = \int \left( \frac{[M]}{[M]_0} \right)^{-\frac{1}{m}} \left[ 2k_p [M]_0 C_1 \left( \frac{[M]}{[M]_0} \right)^2 + 2k_p [M]_0 C_2 \left( \frac{[M]}{[M]_0} \right)^{1+\frac{1}{m}} \right. \\ \left. + \frac{fk_d}{2k_t} (Z+1) 2k_p [M]_0 \left( \frac{[M]}{[M]_0} \right) \right] dt$$

Expressing  $\left( \frac{[M]}{[M]_0} \right)$  in terms of  $(Z_0 - Z)$  and making use of eqn

(A1.4) and dividing by integrating factor, we obtain for the second integral

$$\begin{aligned}
 I_2 = & - \frac{4k_p [M]_0 C_1}{fk_d} e^{-2m(z_0 - z)} \sum_{n=0}^{\infty} \frac{1}{z_0^{n+1}} \sum_{r=0}^n \frac{n!(z_0 - z)^{n-r}}{(n-r)!(2m-1)^{r+1}} \\
 & - \frac{4k_p [M]_0 C_2}{fk_d} e^{-(m+1)(z_0 - z)} \sum_{n=0}^{\infty} \frac{1}{z_0^{n+1}} \sum_{r=0}^n \frac{n!(z_0 - z)^{n-r}}{(n-r)!(m-1)^{r+1}} \\
 & - \frac{2k_p [M]_0}{k_t} \left[ \frac{e^{-(m)(z_0 - z)}}{(m-1)} \right] \\
 & - \frac{2k_p [M]_0}{k_t} e^{-(m)(z_0 - z)} \sum_{n=0}^{\infty} \frac{1}{z_0^n} \sum_{r=0}^n \frac{n!(z_0 - z)^{n-r}}{(n-r)!(m-1)^{r+1}} \quad (A1.13)
 \end{aligned}$$

Similarly the third Integral  $I_3$  is

$$I_3 = - \frac{[M]_0}{1 - \frac{1}{m}} \left( \frac{[M]_0}{[M]_0} \right) \quad (A 1.14)$$

For the sake of convenience, let

$$\sum^2(x) = \sum_{n=0}^{\infty} \frac{1}{z_0^{n+1}} \sum_{r=0}^n \frac{n!(z_0 - z)^{n-r}}{(n-r)!x^{r+1}} \quad (A 1.15)$$

Then

$$\begin{aligned}
 Q_2 = & \frac{fk_d}{2k_t} (z+1) - \frac{4k_p [M]_0 C_1}{fk_d} e^{-2m(z_0 - z)} \sum^2(2m-1) \\
 & - \frac{4k_p [M]_0 C_2}{fk_d} e^{-(m+1)(z_0 - z)} \sum^2(m) - \frac{2k_p [M]_0}{k_t(m-1)} \left( \frac{[M]_0}{[M]_0} \right) \\
 & - \frac{2k_p [M]_0}{k_t} e^{-(m)(z_0 - z)} \sum^2(m-1) - \frac{[M]_0}{1 - \frac{1}{m}} \left( \frac{[M]_0}{[M]_0} \right) + C_2^* \left( \frac{[M]_0}{[M]_0} \right)^{\frac{1}{m}} \quad (A 1.16)
 \end{aligned}$$

$$Q_2 = Q_{20} \text{ at } z = z_0$$

$$\therefore C_2^* = Q_{20} - \frac{fk_d}{2k_t} (z_0 + 1) + \frac{2k_p [M]_0}{k_t(m-1)} + \frac{[M]_0}{1 - \frac{1}{m}} \quad (A 1.17)$$

The differential equation governing second moment of dead polymer distribution (eqn 50) is

$$\frac{d\lambda_2}{dt} = k_t [P] Q_2 + k_{tc} Q_1^2$$

Integrating eqn (51) using eqn (A 1.4) and eqn (30) we obtain on substituting the limits

$$\begin{aligned}
 \int k_{tc} Q_1^2 dt &= \frac{2k_{tc}}{fk_d} \left[ \left( \frac{fk_d}{2k_t} \right)^2 \left\{ \frac{1}{2} \left( z_0^2 - z^2 \right) + 2(z_0 - z) + \ln(z_0 - z) \right\} \right. \\
 &\quad \left. - c_1^2 e^{-2m(z_0 - z)} \sum^2 (2m) + c_2^2 e^{-2(z_0 - z)} \sum^2 (2) \right. \\
 &\quad \left. + c_1 \left( \frac{fk_d}{k_t} \right) \frac{1}{m} (1 - e^{-m(z_0 - z)}) - c_1 \left( \frac{fk_d}{k_t} \right) e^{-m(z_0 - z)} \sum^2 (m) \right. \\
 &\quad \left. + c_2 \left( \frac{fk_d}{k_t} \right) (1 - e^{-(z_0 - z)}) - c_2 \left( \frac{fk_d}{k_t} \right) e^{-(z_0 - z)} \sum^2 (1) \right] \\
 &\quad (A-1.18)
 \end{aligned}$$

## Further

$$\begin{aligned}
 \int k_t [P] Q_2 \, dt &= - \frac{k_t}{k_p} \int \frac{Q_2}{\left( \frac{[CM]}{[CM]} \right)_0} \, d \left( \frac{[CM]}{[CM]} \right)_0 \\
 &= - \frac{k_t}{k_p} \int \frac{Q_2}{\left[ \frac{[CM]}{[CM]} \right]_0} \, d \left( \frac{[CM]}{[CM]} \right)_0 \\
 &= - \int Q_2 \, dz
 \end{aligned}$$

Integrating eqn (A 1.16) using eqn (A 1.4) we get,

$$\begin{aligned}
 \int k_t [P] Q_2 dt &= \frac{fk_d}{2k_t} \left[ \frac{1}{2} \left( z_0^2 - z^2 \right) + 2(z_0 - z) \right] - \frac{3[M]_0}{(m-1)} (1 - e^{-m(z_0 - z)}) \\
 &+ \frac{2k_p [M]_0}{k_t} e^{-m(z_0 - z)} \sum_{(m-1, m)}^3 + \frac{4k_p [M]_0 C_1}{fk_d} \sum_{(2m-1, 2m)}^3 \\
 &+ \frac{4k_p [M]_0 C_2}{fk_d} e^{-(m+1)(z_0 - z)} \sum_{(m, m+1)}^3 + C_2^* (1 - e^{-(z_0 - z)}) \\
 &\quad (A 1.19)
 \end{aligned}$$

Where  $C_2^*$  is as defined in eqn (A 1.17) and

$$\sum_{n=0}^{\infty} (x, y) = \sum_{n=0}^{\infty} \frac{1}{z_0^{n+1}} \sum_{r=0}^n \frac{n!}{(n-r)! x^{r+1}} \sum_{p=0}^{n-r} \frac{(n-r)! (z_0 - z)^{n-r-p}}{(n-r-p)! y^{p+1}} \quad (A1.20)$$

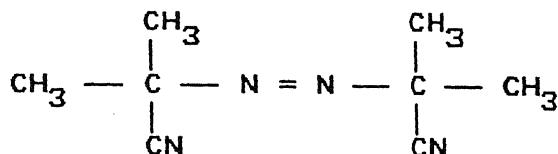
Therefore,

$$\begin{aligned}
 \lambda_2 - \lambda_{20} = & \frac{2k_t c}{fk_d} \left[ \left( \frac{fk_d}{2k_t} \right)^2 \left\{ \frac{1}{2} (z_0^2 - z^2) + 2(z_0 - z) + \ln(z_0 - z) \right\} \right. \\
 & - c_1^2 e^{-2m(z_0 - z)} \sum_{m=0}^2 (2m) - c_2^2 e^{-2(z_0 - z)} \sum_{m=0}^2 (2) \\
 & + c_1 \left( \frac{fk_d}{2k_t} \right) \frac{1}{m} (1 - e^{-m(z_0 - z)}) - c_1 \left( \frac{fk_d}{k_t} \right) e^{-m(z_0 - z)} \sum_{m=0}^2 (m) \\
 & \left. + c_2 \left( \frac{fk_d}{k_t} \right) (1 - e^{-(z_0 - z)}) - c_2 \left( \frac{fk_d}{k_t} \right) e^{-(z_0 - z)} \sum_{m=0}^2 (1) \right] \\
 & + \frac{fk_d}{2k_t} \left[ \frac{1}{2} (z_0^2 - z^2) + 2(z_0 - z) \right] - \frac{3[M]_0 (1 - e^{-m(z_0 - z)})}{(m-1)} \\
 & + \frac{4k_p [M]_0 c_1}{fk_d} e^{-2m(z_0 - z)} \sum_{m=0}^3 (2m-1, 2m) \\
 & - \frac{4k_p [M]_0 c_2}{fk_d} e^{-(m+1)(z_0 - z)} \sum_{m=0}^3 (m, m+1) \\
 & + \frac{2k_p [M]_0 e^{-m(z_0 - z)}}{k_t} \sum_{m=0}^3 (m-1, m) + c_2^* (1 - e^{-(z_0 - z)}) \\
 \end{aligned} \quad (A 1.21)$$

## APPENDIX 2

## Various kinetic models

The bulk polymerization of styrene is carried out in presence of 2,2'-azoisobutyronitrile (AIBN) having the following structure



2,2' azoisobutyronitrile

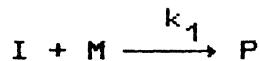
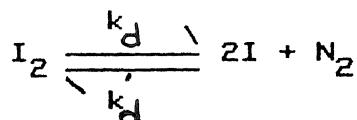
This is stable at room temperature, but decompose thermally above 40°C giving substituted alkyl radials and nitrogen. The radicals remain in a 'cage' before they diffuse apart, and during this time a recombination of radicals may take place. In order to account for this, the initiator efficiency 'f' has been introduced.

We have modelled the cage effect in three different ways to explain the effect of shear upon initiator efficiency 'f' and finally show that the evolved N<sub>2</sub> has a catalytic effect in order to explain the decrease in rate of polymerization of styrene on application of shear.

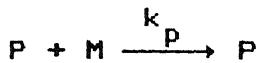
## MODEL 1

The following scheme is proposed:

Initiation:



Propagation:



Termination:



Balance on  $[I]$  gives

$$\frac{d[I]}{dt} = k_d [I_2] - 2 k_d' [I] [N_2] - k_1 [I] [M] \quad (A 2.2)$$

$$\therefore [I] = \frac{k_d [I_2]}{2k_d' [N_2] + k_1 [M]} \quad (A 2.2)$$

Also

$$\frac{d[P]}{dt} = k_1 [I] [M] - k_t [P]^2 \quad (A 2.3)$$

$$\therefore k_t [P]^2 = k_1 [M] \frac{k [I_2]}{2k' [N_2] + k_1 [M]}$$

$$[P] = \sqrt{\frac{k_d [I_2]}{k_t}} \cdot \sqrt{\frac{k_d [M]}{2k_d' [N_2] + k_1 [M]}} \quad (A 2.4)$$

$$r_p = k_p [M] [P] = k_p [M] \sqrt{\frac{k_d [I_2]}{k_t}} \cdot \sqrt{\frac{k_d [M]}{2k_d' [N_2] + k_1 [M]}} \quad (A 2.5)$$

However, we have from eqn (2)

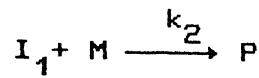
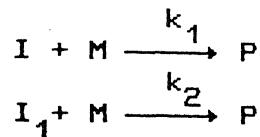
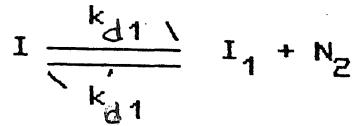
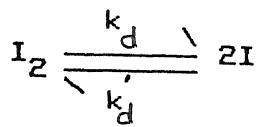
$$r_p = k_p [M] \left( \frac{k_d [I_2]}{k_t} \right)^{\frac{1}{2}} f^{\frac{1}{2}}$$

Hence, on comparing the above two equations, we get

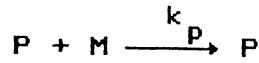
$$f = \frac{k_d [M]}{2k_d' [N_2] + k_1 [M]} \quad (A 2.6)$$

## MODEL 2

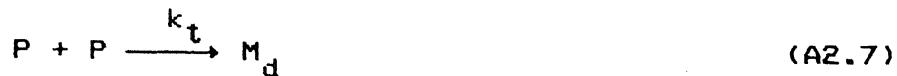
## Initiation



## Propagation



## Termination

Balance on  $[I]$  gives

$$\frac{d[I]}{dt} = k_d [I_2] - 2 k_d [I] - k_{d1} [I] \\ + k_{d1} [N_2] [I_1] - k_1 [I] [M] \quad (A2.8)$$

Balance on  $[I_1]$  gives,

$$\frac{d[I_1]}{dt} = k_{d1} [I] + k_{d1} [N_2] [I_1] - k_2 [I_1] [M] \quad (A2.9)$$

$$\therefore [I_1] = \frac{k_{d1} [I]}{k_{d1} [N_2] + k_2 [M]} \quad (A2.10)$$

$$k [I_2] - 2 k_d [I] - k_{d1} [I] + k_1 [N_2] \frac{k_1 [I]}{k_{d1} [N_2] + k_2 [M]} \\ - k_1 [I] [M] = 0$$

$$\therefore [I] = \frac{k_d [I_2]}{\left[ 2k_d + k_{d1} + k_1 [M] - \frac{k_{d1} k_{d1} [N_2]}{k_{d1} [N_2] + k_2 [M]} \right]} \quad (A2.11)$$

Now,

$$\frac{d[P]}{dt} = k_1 [I] [M] + k_2 [I_1] [M] - k_t [P]^2 \quad (A 2.12)$$

$$[P] = \left\{ k_1 [I] [M] + k_2 [I_1] [M] \right\}^{\frac{1}{2}} \cdot \frac{1}{k_t^{\frac{1}{2}}}$$

$$r_p = k_p [M] [P] = \frac{k_p [M] \{k_1 [I] [M] + k_2 [I_1] [M]\}}{k_t^{\frac{1}{2}}}^{\frac{1}{2}} \quad (A2.13)$$

Let  $x = 2k' + k_1 + k_1 [M] - \frac{k_{d1} k_{d1} [N_2]}{k_{d1} [N_2] + k_2 [M]} \quad (A2.14)$

Then

$$k_1 [I] [M] = k_1 [M] \cdot \frac{k_d [I_2]}{x}$$

$$k_2 [I_1] [M] = k_2 [M] \cdot \frac{k_1 [I]}{k_{d1} [N_2] + k_2 [M]}$$

$$= \frac{k_2 k_{d1} [M]}{k_{d1} [N_2] + k_2 [M]} \cdot \frac{k_d [I_2]}{x} \quad (A 2.15)$$

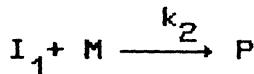
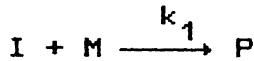
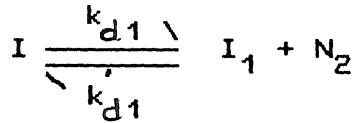
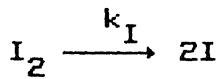
$$\therefore r_p = k_p [M] \left( \frac{k_d [I_2]}{k_t} \right)^{\frac{1}{2}} \left\{ \frac{k_1 [M]}{x} + \frac{k_2 k_{d1} [M]}{x (k_{d1} [N_2] + k_2 [M])} \right\} \quad (A2.16)$$

Comparing the above equation with eqn (2) we get

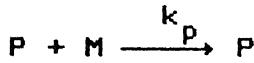
$$f = \frac{k_1 [I]}{x} + \frac{k_2 k_{d1} [M]}{x (k_{d1} [N_2] + k_2 [M])} \quad (A 2.17)$$

## Model 3

## Initiation:



## Propagation:



## Termination:



From  $[I_1]$  balance,

$$[I_1] = \frac{k_{d1}[I]}{k_{d1}[N_2] + k_2[M]} \quad (A2.19)$$

From  $[I]$  balance,

$$[I] = \frac{k_d[I_2]}{Y}$$

$$\text{where } Y = k_{d1} + k_1[M] - \frac{k_{d1}k_{d1}[N_2]}{k_{d1}[N_2] + k_2[M]} \quad (A2.20)$$

From  $[P]$  balance

$$k_t [P]^2 = k_1 [I] [M] + k_2 [I_1] [M]$$

$$k_t [P]^2 = \frac{k_1 k_d [I_2] [M]}{Y} + k_2 [M] \frac{k_{d1} k_I [I_2]}{Y (k_{d1} [N_2] + k_2 [M])}$$

$$[P] = \left[ \left( \frac{k_d [I_2]}{k_t} \right)^{\frac{1}{2}} \frac{k_1 [M]}{Y} + \frac{k_{d1} k_2 [M]}{Y (k_{d1} [N_2] + k_2 [M])} \right]^{\frac{1}{2}} \quad (A2.21)$$

$$r_p = k_p [M] [P]$$

$$= k_p [M] \left( \frac{k_d [I_2]}{k_t} \right)^{\frac{1}{2}} \left[ \frac{k_1 [M]}{Y} + \frac{k_{d1} k_2 [M]}{Y \left( k_{d1} [N_2] + k_2 [M] \right)} \right]^{\frac{1}{2}} \quad (A2.22)$$

Comparing the above equation with eqn (2) we get

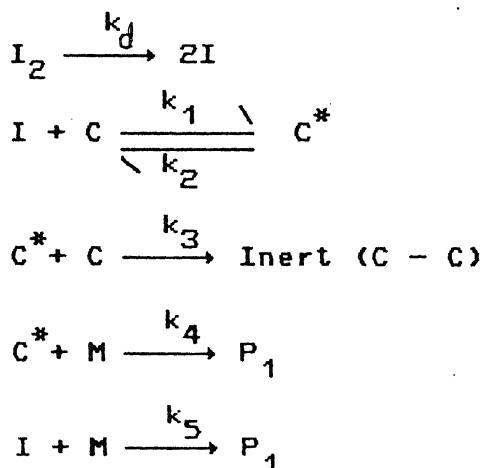
$$f = \frac{k_1 [M]}{Y} + \frac{k_{d1} k_2 [M]}{Y \left( k_{d1} [N_2] + k_2 [M] \right)} \quad (A 2.23)$$

## APPENDIX 3

Model to account for the effect of activated carbon  
on rate of polymerization

It has been found that the rate of polymerization goes up in the presence of activated carbon and the increase appears to depend on the specific surface area ( $\text{ft}^2/\text{ft}^3$ ) of carbon particles used. The following model is put forward to explain the effect of activated carbon concentration on the rate of polymerization;

## Initiation:



## Propagation :



## Termination :



Above  $\text{C}^*$  is an activated species formed by the reaction of primary radicals with carbon. Assuming a steady state hypothesis (S.S. hypothesis) for  $\text{C}^*$ , we get

$$k_1[\text{C}][\text{I}] - k_2[\text{C}^*] - k_3[\text{C}^*][\text{C}] - k_4[\text{C}^*][\text{M}] = 0$$

$$\text{or } [\text{C}^*] = \frac{k_1[\text{C}][\text{I}]}{k_2 + k_3[\text{C}] + k_4[\text{M}]} \quad (\text{A3.2})$$

Balance on  $[I]$  gives (assuming S.S. hypothesis for intermediate species)

$$k_d [I_2] - k_1 [I] [C] + k_2 [C^*] - k_5 [I] [M] = 0$$

Further if we assume that the interaction of initiator radical and carbon particles is small in comparison to decomposition of initiator and formation of  $[P_1]$  we get

$$[I] = \frac{k_d [I_2]}{k_5 [M]} \quad (A 3.3)$$

The rate of polymerization is then given by

$$r_p = k_4 [C^*] [M] + r_{po} \quad (A 3.4)$$

Where  $r_{po}$  is the rate of polymerization in absence of activated carbon.

From eqn (A3.2) we get

$$r_p - r_{po} = \frac{k_4 k_1 [C] [I] [M]}{k_2 + k_3 [C] + k_4 [M]} \quad (A 3.5)$$

$$\frac{1}{r_p - r_{po}} = \frac{k_2 + k_4 [M]}{k_1 k_4 [C] [I] [M]} + \frac{k_3}{k_1 k_4 [I] [M]}$$

On substituting for  $[I]$  from eqn (A 3.3) we get

$$\frac{1}{r_p - r_{po}} = \frac{k_2 + k_4 [M]}{\frac{k_1 k_4 k_d}{k_5} [I_2] [C]} + \frac{k_3}{\frac{k_1 k_4 k_d}{k_5} [I_2] [M]} \quad (A 3.6)$$

If only  $[C]$  is varied, with initiator and monomer concentration remaining almost the same, we can write

$$\frac{1}{r_p - r_{po}} = \frac{k_1^*}{[C]} + k_2^* \quad (A 3.7)$$

$$\text{where } k_1^* = \frac{k_2 + k_4 [M]}{\frac{k_1 k_4 k_d}{k_5}} \quad (a)$$

$$k_2^* = \frac{k_3}{\frac{k_1 k_4 k_d}{k_5} [I_2]_{\text{CM}}}$$

(b) (A 3.8)

A plot of  $\frac{1}{r_p - r_{p0}}$  versus  $\frac{1}{[C]}$  is found to be linear and is included under results and discussion.

Table 1

Mole and energy balance relation for various species in batch (or tubular) reactors carrying out Radical Polymerization

(1) Initiator,  $I_2$

$$\frac{d[I_2]}{dt} = - fk_d[I_2] \quad (1.1)$$

(2) Growing Polymer radicals,  $[P_n]$ , of chain length  $n$  ( $n=1, 2, 3, \dots$ )

$$[P] = \sum_{n=1}^{\infty} [P_n]$$

$$\frac{d[P_1]}{dt} = k_I[I][M] - k_p[P_1][M] - k_t[P_1][P] \quad (1.2)$$

$$\frac{d[P_n]}{dt} = k_p[M] \left[ [P_{n-1}] - [P_n] \right] - k_t[P_n][P] \quad (1.2)$$

3. Monomer,  $M$

$$\frac{d[M]}{dt} = - k_p[P][M] \quad (1.3)$$

4. Inactive Polymer,  $[M_n]$ , of chain length  $n$  ( $n=2, 3, \dots$ )

$$\frac{d[M_n]}{dt} = \frac{k_{tc}}{2} \sum_{m=1}^{n-1} [P_m][P_{n-m}] + k_{td} \sum_{n=1}^{\infty} [P_n] \quad (1.4)$$

5. Energy balance

$$\rho C_p \frac{dT}{dt} = (-\Delta H_r) k_p [M][P] - \frac{4U}{D} (T - T_w) \quad (1.5)$$

Table 2 : Differential Equations for free radical polymerization

1.  $\frac{d[I_2]}{dt} = -fk_d[I_2]$  (2.1)

2.  $\frac{d[P]}{dt} = 2fk_d[I_2] - k_t[P]^2$  (2.2)

3.  $\frac{d[M]}{dt} = -k_p[P][M]$  (2.3)

4.  $\frac{d\lambda_o}{dt} = (0.5k_{tc} + k_{td})[P]^2$  (2.4)

5.  $\frac{dQ_1}{dt} = 2fk_d[I_2] - k_t[P]Q_1 - k_p[M][P]$  (2.5)

6.  $\frac{d\lambda_1}{dt} = (k_{tc} + k_{td})[P]Q_1$  (2.6)

7.  $\frac{dQ_2}{dt} = 2fk_d[I_2] + k_p[M](2Q_1 + [P]) - k_t[P]Q_2$  (2.7)

8.  $\frac{d\lambda_2}{dt} = (k_{tc} + k_{td})[P]Q_2 + k_{tc}Q_1^2$  (2.8)

9.  $\frac{dT}{dt} = \frac{(-\Delta H_r)k_p[M][P]}{\rho C_p} - \frac{4U}{D\rho C_p} (T - T_w)$  (2.9)

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Table 3 : Rate constants and other parameters for PMMA

A	=	$0.168 - 8.21 \times 10^{-6} (T - T_{gP})^2$
B	=	0.03
C <sub>P</sub>	=	0.4 cal/gm°C
E <sub>d</sub>	=	30.66 Kcal/mole
E <sub>p</sub>	=	4.35 Kcal/mole
E <sub>t</sub>	=	0.701 Kcal/mole
E <sub>γ</sub>	=	4.09 Kcal/mole
E <sub>θp</sub>	=	28.2 Kcal/mole
E <sub>θt</sub>	=	34.4 Kcal/mole
f	=	0.58
ΔH <sub>r</sub>	=	13.9 Kcal/mol
k <sub>d</sub> <sup>0</sup>	=	$6.32 \times 10^{16} \text{ min}^{-1}$
k <sub>t</sub> <sup>0</sup>	=	$5.88 \times 10^9 \text{ lit/mol min}$
k <sub>p</sub> <sup>0</sup>	=	$2.95 \times 10^7 \text{ lit/mol min}$
k <sub>γ</sub> <sup>0</sup>	=	$3.956 \times 10^{-4}$
T <sub>gP</sub>	=	387 K
θ <sub>p</sub> <sup>0</sup>	=	$5.4814 \times 10^{-16} \text{ min}$
θ <sub>t</sub> <sup>0</sup>	=	$1.1553 \times 10^{-227} \text{ mol-min/lit}$
ρ <sub>m</sub>	=	$0.9665 - 0.0011 (T - 273) \text{ gm/cm}^3$
ρ <sub>p</sub>	=	$1.2 \text{ gm/cm}^3$
[I <sub>2</sub> ] <sub>0</sub>	=	0.0258 gmoles/lit
[M] <sub>0</sub>	=	8.9334 gmoles/lit

Table 4 : Stable time step for fourth order Runge Kutta Method

Time (min)	$\Delta t=0.02\text{min}$		$\Delta t=0.01\text{ min}$		$\Delta t=0.005\text{ min}$		$\Delta t=0.0001\text{ min}$	
	[P]	$\lambda_0$	[P] $\times 10^7$	$\lambda_0 \times 10^4$	[P] $\times 10^7$	$\lambda_0 \times 10^4$	[P] $\times 10^7$	$\lambda_0 \times 10^4$
10	-	-	0.2175	0.1305	0.83503	0.1299	0.83503	0.1299
20	-	-	0.2193	0.2607	0.8349	0.26066	0.8349	0.2606
30	-	-	0.2210	0.3906	0.8348	0.39132	0.8348	0.3913
40	-	-	0.2228	0.5201	0.8347	0.5219	0.8347	0.5219
50	-	-	0.2245	0.6492	0.8346	0.65256	0.8346	0.6525
60	-	-	0.2263	0.7780	0.83446	0.7831	0.83446	0.7831

Table 5 : Results of Isothermal Polymerization without gel effect  
 (Results in parenthesis are numerical computations with  $\Delta t=0.0001$  min)

Time [M] $\times 10^{-7}$	[P] $\times 10^7$	$Q_1 \times 10^3$	$Q_2$	$\lambda_0 \times 10^3$	$\lambda_1$	$\lambda_2 \times 10^{-4}$	PDI	
10	0.8631	0.834	0.1745	0.7297	0.1306	0.3019	0.1386	1.9851
	(0.8632)	(0.834)	(0.1745)	(0.7297)	(0.1305)	(0.3016)	(0.1385)	(1.9864)
20	0.8340	0.8328	0.1686	0.6822	0.2608	0.5933	0.2682	1.9869
	(0.8341)	(0.8328)	(0.1686)	(0.6823)	(0.2607)	(0.5930)	(0.2680)	(1.9873)
30	0.8059	0.8317	0.1629	0.6379	0.3907	0.8746	0.3892	1.9879
	(0.8060)	(0.8317)	(0.1629)	(0.6380)	(0.3905)	(0.8741)	(0.3890)	(1.9882)
40	0.7788	0.8305	0.1574	0.5965	0.5203	1.1461	0.5022	1.9892
	(0.7788)	(0.8305)	(0.1574)	(0.5966)	(0.520)	(1.1454)	(0.5019)	(1.9895)
50	0.7526	0.8294	0.1521	0.5579	0.6495	1.4081	0.6077	1.9908
	(0.7527)	(0.8294)	(0.1521)	(0.5580)	(0.6492)	(1.4072)	(0.6074)	(1.9910)
60	0.7273	0.8283	0.1470	0.5218	0.7784	1.6610	0.7063	1.9929
	(0.7274)	(0.8283)	(0.1470)	(0.5219)	(0.7780)	(1.6599)	(0.7059)	(1.9930)

Table 6 : Results of Nonisothermal Polymerization without gel effect  
(Results in parenthesis are numerical computations with  $\Delta t=0.0001\text{min}$ )

$$U = 2.0343 \times 10^{-3} \frac{\text{Kcal}}{\text{hr cm}^2 \text{C}}$$

Dia = 2.0 cm

Time (min)	Temp. °K	$[M] \times 10^{-1}$ <u>gmoles</u>	$[P] \times 10^7$ <u>gmoles</u>	$Q_1 \times 10^3$ lit	$Q_2$ lit	$\lambda_0 \times 10^3$	$\lambda_1$	$\lambda_2 \times 10^4$	PDI
10	331.32 (331.49)	0.8687 (0.8662)	0.6631 (0.7529)	0.1707 (0.1707)	0.8791 (0.7742)	0.09047 (0.1142)	0.2454 (0.2718)	0.1329 (1.1332)	1.9897 (1.9864)
20	331.27 (331.44)	0.8462 (0.8405)	0.6575 (0.749)	0.1662 (0.1655)	0.8595 (0.7315)	0.1716 (0.2151)	0.4714 (0.5218)	0.2575 (0.2572)	1.982 (1.9863)
30	331.23 (331.39)	0.8244 (0.8159)	0.6531 (0.7456)	0.1617 (0.1605)	0.8013 (0.6912)	0.2515 (0.3191)	0.6893 (0.7749)	0.3755 (0.3738)	1.9876 (1.987)
40	331.184 (331.342)	0.8034 (0.7920)	0.6487 (0.7423)	0.1575 (0.1557)	0.7648 (0.6531)	0.3303 (0.4221)	0.900 (0.1013)	0.4874 (0.4835)	1.9874 (1.9874)
50	331.146 (331.296)	0.7830 (0.7689)	0.6446 (0.7392)	0.1534 (0.1510)	0.7302 (0.6174)	0.40809 (0.5242)	0.1104 (0.1243)	0.5936 (0.5868)	1.9876 (1.9883)
60	331.110 (331.252)	0.7633 (0.7467)	0.6407 (0.7361)	0.1495 (0.1466)	0.6772 (0.5837)	0.4849 (0.6254)	0.1301 (0.1466)	0.6942 (0.68403)	1.988 (1.989)

TABLE 7

Effect of Shear on Rate of Polymerisation in Absence of Activated Carbon

$[M] = 8.356$  gmoles/lit       $\rho_m$  at  $60^\circ C = 0.869$  gm/cc

$[I_2] = 0.0533$  gmoles/lit       $\rho_{ps}$  at  $60^\circ C = 1.0475$  gm/cc

RPM	$\gamma = \frac{\omega R_R}{R_G - R_R}$ $\text{sec}^{-1}$	Slope $\times 10^3$ lit/min	$Y \times 10^5$ lit gmoles min	$r_p \times 10^4$ gmoles lit min	$Z$
0	0.0	4.28	8.466	1.627	0.9995
50	36.48	3.89	7.902	1.514	0.9985
100	72.96	3.41	6.876	1.327	0.9917
130	94.85	3.19	6.407	1.245	0.9964
165	120.39	3.55	6.908	1.348	0.9988
200	145.92	3.76	7.451	1.430	0.9935
250	182.40	4.35	8.820	1.694	0.9991

TABLE 8

Effect of Shear on Rate of Polymerisation in Presence of  
Activated Carbon

Carbon Concentration: 100 mg/200 ml monomer

$[M] = 8.356$  gmoles/lit  $\rho_m$  at  $60^\circ C = 0.869$  gm/cc

$[I_2] = 0.05275$  gmoles/lit  $\rho_{ps}$  at  $60^\circ C = 1.0475$  gm/cc

RPM	$\gamma = \frac{\omega R}{R_G - R}$ $\text{sec}^{-1}$	Slope $\times 10^3$ lit/min	$\frac{Y \times 10^5}{\text{lit}^0.5 \text{gmoles}^{-0.5} \text{min}^0.5}$	$r_p \times 10^4$ gmoles lit min	$R^2$
0	0.0	5.0	10.17	1.940	0.9947
50	36.48	3.59	7.267	1.399	0.9995
75	54.72	4.19	9.017	1.711	0.9997
100	72.96	4.99	10.37	1.989	0.9850
150	109.44	4.63	9.307	1.800	0.9992
180	131.33	4.69	9.565	1.824	0.9968

TABLE 9

Effect of Activated Carbon (-350 mesh size) on  
Rate of Polymerization

$[C] = 8.356$  gmoles/lit       $\rho_{ps}$  at  $60^\circ C = 1.0475$  gm/cc  
 $\rho_m$  at  $60^\circ C = 0.869$  gm/cc

$\frac{[C]}{2} \times 10^2$ gmoles	$\frac{1}{[C]} \frac{1}{2}$ lit	$\frac{[I_2]}{2}$ gmoles	Slope $\frac{3}{2} \times 10^3$ lit/min	$Y \times 10^4$	$\frac{r_p}{4} \times 10^4$ gmoles/lit min	$\frac{1}{r_p - r_{p0}}$ lit/min	$\frac{2}{R}$
lit	gmoles	lit	min		lit min	gmoles	
0	$\infty$	0.037	3.868	0.983	1.580	-	0.997
1.66	60	0.038	4.582	1.114	1.826	40650.4	0.996
2.33	42.86	0.037	4.300	1.088	1.757	56657.2	0.999
2.66	37.50	0.038	4.560	1.085	1.773	51948.1	0.999
3.33	30.00	0.038	4.520	1.130	1.846	37664.2	0.998
6.00	16.67	0.037	5.220	1.331	2.133	18099.5	0.999

TABLE 10

Effect of Activated Carbon (-250 mesh size) on  
Rate of Polymerization

$[M] = 8.356$  gmoles/lit

$\rho_{ps}$  at  $60^{\circ}C = 1.0475$  gm/cc

$\rho_m$  at  $60^{\circ}C = 0.869$  gm/cc

$\frac{[C]}{2} \times 10^2$ gmoles	$\frac{1}{[C]}$ lit	$\frac{[I_2]}{2}$ gmoles	Slope $\times 10^3$ lit/min	$Y \times 10^4$	$\frac{r_p}{4} \times 10^4$ gmoles lit min	$\frac{1}{r_p - r_{p0}}$ lit min	$\frac{2}{R}$
0.00	$\infty$	0.037	3.868	0.983	1.581	-	0.997
1.66	60	0.037	3.960	1.009	1.618	266666.7	0.999
2.00	50	0.037	3.952	1.010	1.615	289855.0	0.993
2.33	42.86	0.037	3.822	0.962	1.562	- .	0.997
3.00	33.33	0.039	4.390	1.087	1.794	46838.4	0.999
3.66	27.27	0.038	4.170	1.047	1.704	80775.4	0.999

Table 11

Gel and Glass effect constitutive equations

$$k_t = \frac{k_{t0} D_0}{D_0 + k_{t0} \theta_t \lambda_0} \quad (\text{gel effect}) \quad (11.1)$$

$$k_p = \frac{k_{p0} D_0}{D_0 + k_{p0} \theta_p \lambda_0} \quad (\text{glass effect}) \quad (11.2)$$

where

$$\theta_t = \frac{\theta_t^0}{[I_2]} \exp(E_{\theta_t}/RT) \quad (11.3)$$

$$\theta_p = \frac{\theta_p^0}{[I_2]} \exp(E_{\theta_p}/RT) \quad (11.4)$$

$$D_0 = \left[ \frac{2.303(1-\phi_p)}{A + B(1-\phi_p)} \right] \quad (11.5)$$

$$\gamma = \frac{k_{tc}}{k_{td}} = \frac{k_\gamma^0}{[I_2]} \exp(E_\gamma/RT) \quad (11.6)$$